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DEVELOPMENT OF CHARACTERIZED AND REPRODUCIBLE SYNTACTIC FOAM OF PHENOLIC NYLON FOR HEAT SHIELDS

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HUGHES AIRCRAFT COMPANY
CULVER CITY, CALIFORN

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FINAL REPORT

for

DEVELOPMENT OF CHARACTERIZED AND REPRODUCIBLE
SYNTACTIC FOAM OF PHENOLIC NYLON FOR HEAT SHIELDS

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FOREWORD

This report was prepared by Hughes Aircraft Company on the work performed under Contract NAS 2-2739 "Development of Characterized and Reproducible Syntactic Foam of Phenolic Nylon." The work was administered under the direction of the Gas Dynamics Division, Ames Research Center, National Aeronautics and Space Administration, with Dr. John Parker as Project Engineer.

This report covers work done from 1 February 1965 to 31 December 1965.

ABSTRACT

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This report describes the characterization and improvement of low density syntactic foam based on phenolic resin and 40 percent powdered nylon. The work was carried out in two concurrent phases.

In the first phase, existing nylon phenolic foam designated for use as an ablative heat shield in the Scout Re-Entry program was studied to determine its properties and uniformity. Also, the reproducibility of the materials and processes used in the manufacture of the Scout Nosecap were investigated intensively. The Scout re-entry material was found uniform and reproducible in its bulk physical properties but heterogeneous and highly porous in its microstructure.

In the second phase, methods of upgrading raw materials and processes to produce an improved, more uniform nylon phenolic ablator were investigated. This work culminated in a revised formulation containing upgraded raw materials which was molded directly into the Scout Nosecap configurations by a new process. The microstructure of the improved material was considerably more uniform than its forerunner. Porosity was reduced, compressive strength increased twofold and tensile strength increased fourfold.

This work has shown that uniformity of microstructure and the reduction of interconnected porosity improve the physical properties of low density ablators. The methods developed for improving the raw materials and molding shapes of low density nylon phenolic materials are suitable for scaling up to large sizes.

ILLUSTRATIONS

1.0 INTRODUCTION

Low density ablative materials have been demonstrated to be very effective ablators (Reference 1) and are of great interest for the thermal protection of vehicles during reentry into both terrestrial and extra-planetary atmospheres. The high performance of these materials appears to be due to a combination of several factors among which are (1) very low thermal conductivity, (2) the ready incorporation of pneumagenic materials which produce low molecular weight gases, and (3) the ability to produce stable and permeable chars.

The low density ablators studied in this program are rigid molded materials of approximately thirty five pounds per cubic foot density. All of the formulations contained forty percent by weight of finely powdered nylon. The function of the nylon is to produce large volumes of low molecular weight gases during ablation. Little or no carbonaceous char is produced by the thermal degradation of the nylon.

The balance of the ablative formulation consists of two chemically similar components, a resinous matrix or binder, and a void producer. The resinous matrices are thermosetting resins of the phenolic novolac type. The function of the resin matrix is twofold, first to bind all of the ingredients together to produce a strong and useful structure, and second, to form a stable but porous char during ablation. The third ingredient in these ablative formulations is hollow microspheres (Ref. 2) of phenolic resin. The primary function of this precured low density material is to produce voids in the final product in an ordered and controlled manner. Materials incorporating these spheres are termed syntactic foams based on the dictionary definition of syntactic---- "Connected system or order; orderly arrangement." Since the walls of the microspheres are of similar chemical nature to the phenolic resin matrix they also contribute to char formation during ablation.

The manufacture of the ablative material consists of:

1. dry blending the three finely powdered ingredients
2. compression molding under heat and pressure to reduce
    the bulk and cure the resin matrix
3. postcuring the molded material at elevated temperature to
    assure full cure and thermal stability.

The process for molding the ablative materials is complicated
by several difficulties inherent in the raw materials and the mixture.
Among these are the very high bulk of the uncured mixture, the
fragility of the microspheres, and the low thermal conductivity of both
the uncured mixture and cured product. These difficulties combined
with lack of knowledge of the properties and variability of the raw
materials cast serious doubt on the quality and reproducibility of the
finished product.

This program was initiated to investigate the uniformity and
reproducibility of the nylon phenolic syntactic foam intended for use in
the Nosecap for the Scout re-entry vehicle. In the Scout program,
calculated ablation performance based upon laboratory measurements
of material properties is compared with actual in-flight ablation per-
formance. Therefore in order to have a controlled experiment it was
essential that variability of properties between and within Nosecaps be
kept to a minimum. In order to determine the variability of the
material (produced by the Langley Research Center) it was necessary
to:

*   Characterize the properties of the raw materials and
    the finished product.
*   Establish the variability of significant properties of
    the raw materials and finished product.
*   Investigate the process and the degree of process control
    used in making the finished ablator.
*   Establish specifications containing realistic tolerances
    for the raw materials and finished product.

In addition to the effort of characterizing and establishing the variability of the present Scout Nosecap material a parallel effort was performed. This task consisted of producing an improved and more closely controlled nylon syntactic foam based on the original formulation. Using the understanding and data developed in characterizing of the Scout material several avenues of improvement were predicted and applied. The improvements were based on the following approaches:

1. upgrading the raw materials
2. increasing the uniformity of the microstructure
3. modifying the formulation
4. developing a process which reduces the physical damage to the phenolic microspheres during molding

The modification of the ablative materials and process resulted in:

1. uniform and controllable properties in the raw materials, and in the micro and macro structure of the cured material
2. reduction of microsphere damage
3. reduction of the ratio of interconnected to discrete voids
4. stronger material

All of the tasks were carried to conclusion in a period of ten months. Much of the work was performed in an intensive manner for integration with a tight NASA schedule. The characterization of the Langley material revealed that it was uniform in bulk physical properties but heterogeneous and highly porous in its micro structure. Simple techniques were developed for improving the quality and reproducibility of the raw materials. Analysis of the function and the volume fraction relationships of the raw materials in the final product revealed that the Langley formulation was not optimum. In addition, the method of processing was deleterious and limited in utility.

An upgrading effort culminated in a material of greatly improved physical properties and more uniform microstructure. The new process molded the Nosecaps to size (Fig. 1), thereby eliminating machining and the necessity of molding oversize billets. The use of

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Figure 1.   Molding of Scout Re-Entry Nosecaps showing press, mold and dielectric preheater.

dielectric pre-heating and rapid curing presents the possibility of scale-up of the process to very large shields.

Particularly significant in this development is the demonstration that optimization and control of processing conditions can be accomplished without major modification of the chemical nature of a formulation.   Also, the mathematical analysis of the volume relationships of the constituents in the formulation and the use of these relationships to predict optimum formulations promises to be an extremely useful tool.   The method of analysis should apply to the optimization of all low density ablative materials and eventually to all multiphase polymeric materials.

2.0 CHARACTERIZATION OF THE EXISTING NYLON PHENOLIC SYNTACTIC FOAM

The material used in the Nosecap for the Scout Re-entry vehicle is a low density composition based on powdered nylon and phenolic resin. The low density of 35 pounds per cubic foot is obtained by incorporating hollow microspheres of cured phenolic resin. The microspheres are presumed to introduce gas filled voids in the material in an ordered manner. For this reason the material is called a syntactic foam.

The formulation of the Langley ablative material is as follows:

40% by weight powdered nylon – 80 mesh average

35% by weight of phenolic microspheres

25% by weight of powdered phenolic novolac resin – 240 mesh

The ingredients in the formulation are all fine powders of a fluid nature. They are mixed in the correct proportion on the basis of dry weight and subjected to a gentle blending action in a Vee Blender. The mixture is then charged into a cold mold of cylindrical shape. The charge is subjected to pressure, a vacuum is applied to the mold interior, and the pressure is then relaxed. The mold temperature is then increased to approximately 325°F and the part cured for approximately 20 hours. The resulting billet is 13 inches in diameter and approximately 4 1/2 inches high. After subjecting the billet to an extended postcure in inert atmosphere, the Scout Nosecap is machined to the shape shown in Figure 2.

In order to characterize the molded billet material, to understand the sources of variability, and to improve the product, the first phase of the investigation was broken down into five areas of study.

1. Raw materials
2. Process
3. Billet material
4. Interaction of materials and process
5. Analysis of results
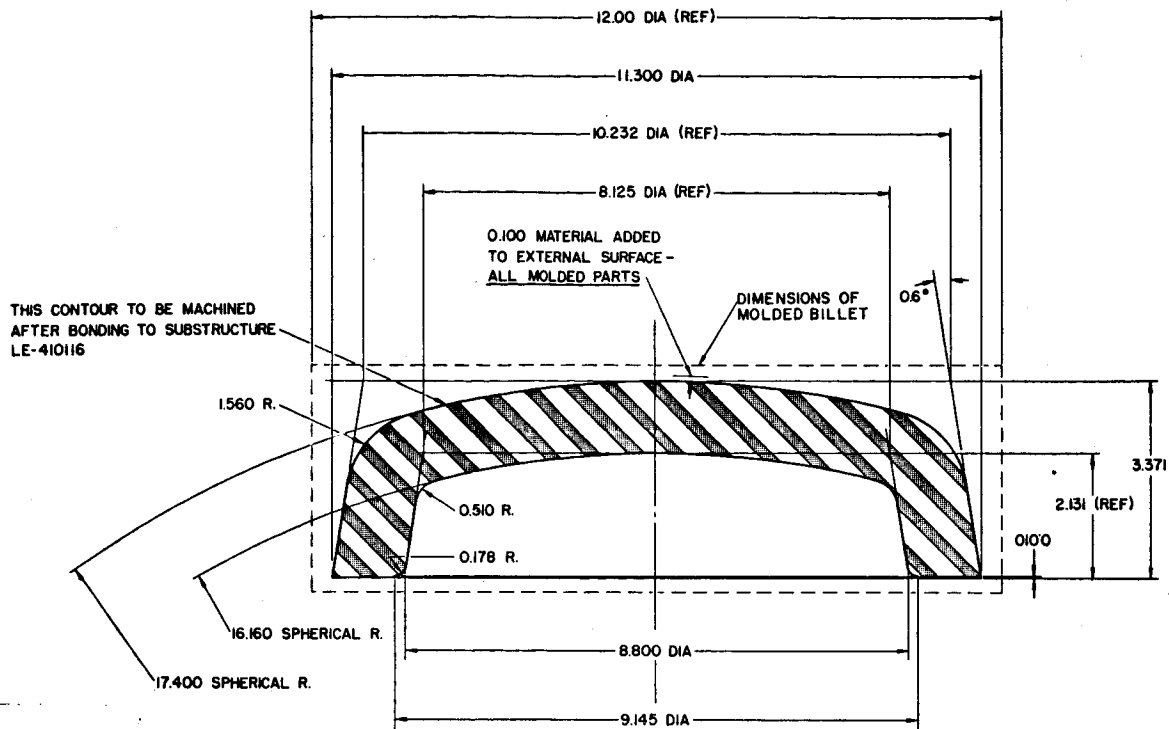
Figure 2.   Scout Nosecap and billet drawing.

A primary concern of the contractor was the variability of both the bil-
let material and of the raw materials.   Since the molded billet mate-
rial was intended for use as an ablative standard it was considered essen-
tial that assurance of future uniformity be established.   In order to
attain an accurate measure of these factors, statistical sampling tech-
niques and analyses were used wherever possible.

For each of the raw materials and for the billet material it was
therefore necessary to follow the following investigation procedure.

1.   Determine the basic properties of the material

2.   Select meaningful and sensitive tests and procedures

3.   Establish a statistical sampling and testing plan

4.   Perform measurements

5.   Analyze the data

In some cases it was necessary to develop special non-standard tests to obtain information significant to this unusual product. All special test procedures are fully detailed in Appendix I.

2.1 GENERAL DESCRIPTION OF RAW MATERIALS

2.1.1 Phenolic Novolac

A phenolic novolac resin is a condensation polymer formed by the reaction of phenol and formaldehyde. The reaction is carried out with an acid catalyst (generally oxalic acid) usually in aqueous solution. A molar excess of phenol to formaldehyde is required to produce a true novolac (Ref. 4). The product is a thermoplastic resin consisting primarily of a straight chain polymers of phenolic nuclei linked by ortho and para positions. The polymer may be represented in a highly idealized fashion as shown (Ref. 5).
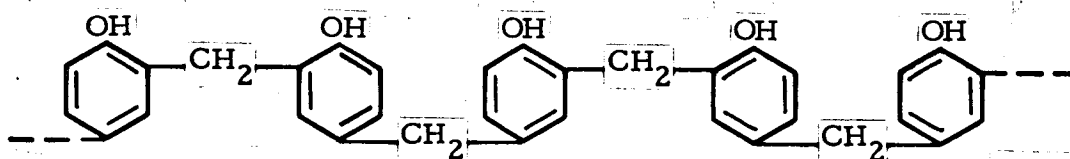
The thermoplastic novolac polymer may be converted to an infusible cross linked polymer by the addition of additional sources of methylene leakages. In practice this is done by the addition of hexamethylene tetramine which is illustrated below.

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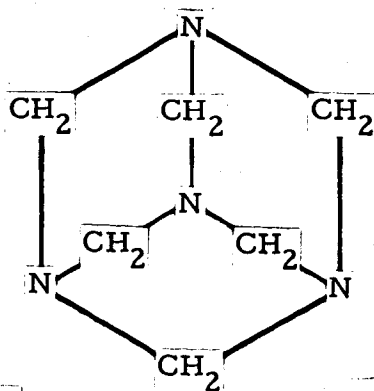
The hexa is intimately ground with the solid novolac resin. Upon curing the resin in the temperature range of 150 to 180°C, the hexa decomposes. This provides an additional source of methylene linkages and liberates ammonia which serves as an alkaline catalyst. The final reaction is similar to resole formation and results in a highly cross linked infusible product. Products of the novolac type of phenolic polymer are therefore termed two-step resins because of the two distinct reaction steps required to bring them to a fully cured infusible form.

Commercial novolac resins therefore consist of a mixture of finely ground thermoplastic phenolic resin and hexamethylene tetramine. The resin usually has a number average molecular weight of 650-800 in which the chemical constituents may range from unreacted phenol to polymer chains having as many as twelve phenol nuclei.

The novolac resin used in the Langley formulation is a typical commercial novolac developed primarily as a foundry resin for bonding sand cores and molds used in metal casting. The properties of the resin as published in the manufacturer's brochure are shown in Table 1.

Property	Testing Method	Unit	Required Value
Plate Flow	WC-627-C	mm	20-45
Powder Density	WC-2B-1	gms/cc	0.27 - 0.31
Hexa Content	WC-115-A-1	per cent	8.7 - 9.5
Sieve Analysis	WC-7-D		
(U.S. Std. Screens)			
On 40 mesh		per cent	0.0
On 100 mesh		per cent	0.6 max
On 200 mesh		per cent	2.0 max cumulative
Thru 200 mesh		per cent	98.0 min.

Table 1. Manufacturer's specification for phenolic novolac.

The manufacturer reported that the resin is prepared in very large batches of 5,000 - 10,000 pounds at extended intervals. A new batch is made up only when the supply from the previous batch runs low. It was not possible therefore to obtain samples of more than one batch of the resin because only the single large batch was available at the time of the investigation.

A discussion of probable sources of variability in phenolic novolac resins and the other raw material is given in Appendix II.

2.1.2 Phenolic Microspheres

This product is a lightweight reddish powder consisting of microscopic hollow spheres of cured phenolic resin. The spheres have an average diameter of 0.0017 inch and are filled with inert gas, primarily nitrogen, during manufacture. It is presumed that the phenolic resin used is of the resole type.

The specifications for the microspheres as given by the manufacturer are shown in Table 2.

Density (Liquid displacement)	0.25 gm/cc max. (15.6 lbs/ft^3)
Density (air displacement)	0.30 gm/cc max. (18.7 lbs/ft^3)
Flotation in Toluene Dupanol Solution	Not less than 90% shall float
Average Particle Size (dia) Size Range (dia.)	0.0017 inch 0.002 to 0.0005 inch

Table 2. Manufacturer's specification for phenolic microspheres.

2.1.3 Nylon

The powdered nylon used in the Langley formulation is of Nylon 66 type, i.e., it is a linear polymer based on the reaction of hexamethylene diamine $H_2N(CH_2)_6 NH_2$, and adipic acid, $HOOC(CH_2)_4COOH$. The nylon molding powder is ground at low temperature in liquid nitrogen to average 80 mesh particle size. The nylon also contains a small percentage of heat stabilizer to retard

embrittlement at high temperatures. Nylon 66 polymers of molding grade have an average molecular weight of the order of 12,000.

Typical properties of nylon 66 as listed in the manufacturer's literature are shown in Table 3.

Specific Gravity	1.13 - 1.15
Melting Point (Fisher Johns)	250-260°C
Tensile Strength, Room Temp.	11,800 psi
Coefficient of Linear Thermal Expansion	4.5×10^{-5} in./in./°F
Thermal Conductivity	1.7 BTU/hr/ft^2/°F/in.
Specific Heat	0.3 - 0.5 BTU/lb

Table 3. Manufacturer's data on nylon 66.

2.2 THE PRODUCTION PROCESS FOR LANGLEY BILLETS

The process for the fabrication of molded billets for Scout Reentry Nosecaps is completely detailed in a NASA Langley Procedure No. 104A (Ref. 6). This process document is lengthy and therefore is not included in this report. The major features of the process are given below.

The raw materials are sampled and moisture content is determined. The nylon and phenolic microspheres are then vacuum dried for 3 hours at 200°F. A batch of molding material is then prepared sufficient for a single billet molding and samples according to the following formulation:

25% Phenolic Resin	1287 gm
40% Powdered Nylon	2060 gm
35% Phenolic Microspheres	1803 gm

The weighed raw materials are loaded into a Vee Blender after sifting through a twenty mesh screen and blended for a total of approximately 25 minutes in a precisely specified order. The blended formulation is then ready for molding.

The billet is molded in a simple cylindrical mold mounted in 500 ton hydraulic press. The steel mold is steam heated, has provision for vacuum lines to the cavity, and is instrumented with both thermocouple and pressure transducers.

The molding operation starts by placing a layer of glass cloth in the bottom of the cavity to act as a volatile sink. The molding material is then placed in the cavity and leveled. Additional layers of volatile sink material are placed on the top of the charge. The press is then closed and pressure is exerted on the material to compress it to 7/8 of an inch less than its normal thickness. The pressure exerted is estimated to be of the order of 2000 psi. The material is then allowed to decompress or expand under the dead weight of the top press platen (approximately 2000 lbs total) to a thickness of 4 1/2 inches. The press is then opened and shims are placed on the top mold cavity to act as lands so that the press cannot close past the 4 1/2 inch thickness of the molded billet. The press is then closed at 100 tons load to the lands so that most of the press load is borne by the mold rather than the molding material.

The cure cycle is then begun by steam heating the mold to 335°F. Vacuum is maintained in the mold cavity during this procedure. The cure cycle is specified as three hours at 315°F for the center volume of the molding. After curing, the ablator is cooled to $275^{\circ} \pm 10^{\circ}$F, removed from the mold and placed in an insulated container for 10 hours. The total process time in molding a billet is approximately 24 hours. This complex curing procedure has been presented in a graphical form in Figure 3.

The final step in the fabrication of molded billets is postcuring in an inert atmosphere. The billets are placed in a container having a continual flow of argon gas through it. The temperature is then raised to 300°F at a uniform rate and then maintained at 300°F for six hours. The billets are then cooled to 275°F in the argon atmosphere, removed and placed in a container to cool to room temperature.

The finished ablator billets are then machined by conventional means into finished Scout Nosecaps as shown in Figure 2.
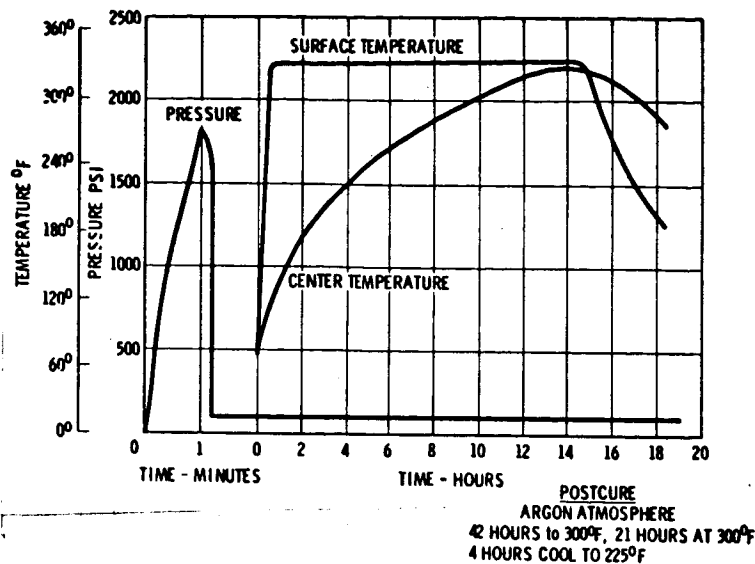
Figure 3. Molding process for Langley billet.

2.3 CHARACTERIZATION OF MOLDED BILLET MATERIAL

2.3.1 Initial Test Development

Preliminary investigations were undertaken to establish test methods used. Methods were selected to provide meaningful data in terms of the use of the material and which would serve as quality control tests. It was considered essential that the tests selected for quality control and variability studies be of sufficient precision to clearly reveal differences in the material tested.

The preliminary tests were begun on a portion of a preproduction billet sent from NASA Langley and on similar material received from NASA Ames. Production billets were not received from NASA Langley until much later in the program, a circumstance which forced eventually a reduction in the planned testing program due to time limitations.

The tests were divided up into these types:

a) Indications of general quality:

Visual and microscopic examination

X-Ray

Machinability

12.

b) Tests suitable for statistical analysis:

    Density

    Compressive strength

    Volatiles and ash content

    Extractable nitrogen (including ammonia)

    Emission spectra of ash

    Porosity

c) Tests indicative of properties but not suitable for statistical analysis:

    Thermogravimetric analysis

    Infrared spectroscopy

The results of these tests are presented in tabular form in Table 4. Details of the tests and test methods are given in Appendix III.

In addition to the tests listed in Table 4 microscopic examinations were made of various machined surfaces. It was found that all methods of machining and polishing caused severe destruction of the microspheres at the surface. It was therefore decided that photomicrographs of these surfaces were meaningless since the surface had been damaged. Later it was found that samples impregnated with epoxide resin and cured (in connection with the Hughes porosity test) could be adequately sectioned and polished. A photomicrograph of such a surface is shown in Figure 4.

Porosity tests had been conducted with success by NASA Langley using the mercury intrusion method (Aminco Porosimeter). Since this equipment was not available at Hughes it was decided to have Aminco perform tests on a limited number of samples and to develop a simple and more economical test for use as a quality control method. It was also decided to use only very low pressures to impregnate the samples to minimize destruction of phenolic microspheres. The test as finally developed consisted of impregnating small ablator samples with a low viscosity epoxide resin, at 50 psi, curing at low temperature, and measuring the increase in weight of the sample. From the data obtained it was possible to calculate the volume percent of continuous

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Material	Test	Method	Results and Comments	No. of Tests
Langley	X-Ray	Industrial	Metal chip located, otherwise uniform	1
Ames	X-Ray	Industrial	Uniform	1
Langley	Density	.505" dia x 1" high specimen	$\bar{x}$ = 36.1 lbs/ft^3, S = ±1.5 lbs/ft^3	12
Ames	Density	.505" dia x 1" high specimen	$\bar{x}$ = 36.0 lbs/ft^3, S = ±0.4 lbs/ft^3	7
Ames	Compressive Strength	1/2 x 1/2 x 1/2" specimen	$\bar{x}$ = 3465 psi, S = ±468 psi	6
Ames	Compressive Strength	.505 dia x 1" specimen	$\bar{x}$ = 3579 psi, S = ±265 psi	7
Langley	Compressive Strength	.505" dia x 1" high specimens	$\bar{x}$ = 5318 psi, S = ±669 psi	12
Ames & Langley	Machinability	- - -	Easily machined, surface friable	2
Ames	Free & combined Ammonia	See Appendix	0.166 - 0.178%	1
Ames	Volatile content	3 hours at 300°F	Top 2.89% Middle 3.37% Bottom 3.47%	1 1 1
Ames	Ash content		Top 1.15% Middle 1.35% Bottom 1.37%	1 1 1

Note: $\bar{x}$ = Mean, S = Standard Deviation

Table 4. Results of preliminary tests on pre-production billet samples.

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Figure 4. Photomicrograph (1000X) of Langley billet microstructure after epoxide resin impregnation.

voids, the volume percent of discrete voids, and the combined or total void content. The Hughes porosity test is fully described in Appendix I.

The results of porosity measurements on the **preproduction bil-**let from Langley are shown in Table 5. The assumption is made in these results that the resin impregnated all continuous (interconnected)

Specimen Number	Original Density gm/cc	Impregnated Density (Cured) gm/cc	Impregnated (Continuous) Void Content as % of Total Void Content
3-A1	0.616	0.951	63.1
3-A2	0.604	0.957	65.2
3-A3	0.597	0.951	64.5
3-A4	0.589	0.938	62.8
3-A5	0.585	0.923	60.5
3-A6	0.578	0.910	58.7
3-A7	0.571	0.889	56.5
3-A8	0.575	0.889	55.3
1-A1	0.604	0.922	58.6
1-A2	0.571	0.934	63.4
1-A3	0.561	0.942	65.5
1-A4	0.557	0.936	64.9
1-A5	0.561	0.950	66.9
1-A6	0.570	0.948	65.9
1-A7	0.614	0.942	61.6
1-A8	0.581	0.953	66.0
Mean			62.46
Standard Deviation			±4.14

Table 5. Porosity of preproduction Langley billet.

voids and that no microspheres are crushed. The figures reveal that the Langley material is highly porous.

Attempts to obtain infrared spectroscopic analyses on finely powdered samples of the pre-production billets were unsuccessful. In all cases the material was too opaque to obtain useful readings.

It was also decided to conduct Thermogravimetric Analyses both at Hughes and at Aminco because of possible differences in the equipment.

2.3.2 The Sampling and Testing Plan for Langley Billets

On the basis of the preliminary test results a sampling plan was set up for the Langley billets. The production plan at Langley called for a continuous run of thirty billets with no change in the process. In the event that a deviation did occur from the standard procedure, that billet was to be eliminated and removed from consideration. Previous to the establishment of the sampling plan, the Langley process had been studied and observed. It was agreed that all reasonable controls were being maintained and that the process was reproducible within narrow limits. A random selection of six billets was therefore made from the total of thirty billets to be produced.

The billets to be tested at Hughes were Numbers 2, 8, 12, 19, 22, and 26.

A sampling plan was set up to determine within billet variation and check the significance of these variations in terms of position within the 12 inch diameter by 4 1/2 inch high cylindrical billets. By this method it should be possible to reveal significant variations in the axial (height), radial, and circumferential directions. The complete sampling and testing plan including that for raw materials and formulation prior to molding is given in Appendix III.

2.3.3 Results of Langley Billet Tests

Due to the fact that the six sample billets from Langley were not all delivered until late in the program, the complete sampling plan was not carried out. However the magnitude of variations between billets and within billets was found to be small and, from the statistical standpoint, it was not considered necessary to exhaustively test and analyze the last three billets.

A summary of data collected is presented in Table 6. A full discussion of the analysis of variance and significance of these results is given in Appendix IV.

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Billet No.	2	8	16	19	22	26
Bulk Density - lbs/ft^3	35.26	35.44	35.28	35.28	35.15	35.32
Appearance	Dark	Light	Mottled	Dark	Dark	Mottled
X-Ray	Uniform	Uniform	-	-	-	-

Table 6. Data on intact billets.

2.3.3.1 Quality Control Tests

Moisture and Density Determinations

Billets Nos. 2 and 8 were machined to provide specimens representative of variations in axial, circumferential and radial locations. A total of 54 density-moisture content specimens were fabricated 3/4" in diameter and 1/2" high. These specimens represented 6 height, 3 radial and 3 circumferential locations.

The individual specimens were weighed and measured both before and after oven exposure of one hour at 325°F. The dimensional characteristics remained constant during drying.

The results of the tests for each of the sets of specimens are shown in Table 7.

Billet No.	Percent Volatiles		Density lbs/ft^3		
	$\overline{X}$	S	$\overline{X}$	S	N
2	3.10	±0.013	33.68	±0.062	54
8	3.46	±0.016	33.44	±0.484	54

Table 7. Density and volatiles content of billets Nos. 2 and 8

The discrepancy between the billet density and the individual specimen mean density can be attributed to two factors:

a. The 3% by weight of volatiles which have been removed.

b. The syntactic foam expands after machining. The effect is thought to be due to the relief to compressive strains induced by the molding operation.

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Analysis of Variance on Density Results

At this point it had become obvious that the magnitude of variation between and within billets was small and that density measurements appeared to be the most precise and useful test for analysis of variance.

The results of the analysis of variance of density data for Billet Nos. 2 and 8 are presented in Appendix IV.

The conclusions of the density study are summarized as follows:

The billets are not homogeneous in density. On the contrary the density varies from point to point within a billet but not in random fashion. Instead the density at a given point is a function of the coordinates of the point. The distribution of densities within a billet can be represented approximately by a model consisting of a low density core encased in a high density shell. The actual density gradient at each point cannot be determined from these data because of the large increments of coordinates selected for study (three levels per factor). However there is evidence, particularly in the case of the radius factor, that the density gradient near the outer surface is quite steep.

It must be emphasized that the above model is only an approximation to the actual situation. As a matter of fact densities vary from point to point within the shell as well as within the core. However the densities of corresponding points of the two billets are correlated.

The behavior of such a molding material under pressure might explain the results qualitatively. A study of the formulation used for making this material reveals that there is insufficient resin to obtain flow as in a conventional molding material. Such being the case it follows as a corollary that we do not have a system in which the molding pressure is constant throughout the mass being molded. This effect plus the more rapid curing of the surface result in non-uniform crushing and compaction.

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Although the material does not conform to the accepted norm of a good molding material, this does not necessarily preclude its being acceptable as an ablative material. The question can be settled conclusively by experimentally determining the relationship between such density heterogeneity and the ablative properties of a material. It can also be anticipated that such factors as compressive strength, porosity, and thermal conductivity will also vary throughout the billets in a similar pattern. These properties may have a more pronounced effect on ablative performance.

It must be emphasized again that although statistically significant and real (i. e., not due to variations in test procedure, etc.) the variations in density are of small magnitude. Furthermore the pattern of variation was clearly defined. It was therefore decided to greatly reduce the sampling and testing of the remaining billets.

Billet No. 12 sampled in a limited fashion to verify the variation of specimens from the outer edge to inner core. Specimens were selected from a single circumferential location. These specimens represented 6 height and 3 radial locations. The 18 moisture-density specimens were 3/4 inch diameter by 1/2 inch high.

The individual specimens were weighed and measured both before and after oven exposure of one hour at 325°F. The dimensional characteristics remained constant during drying. The mean value for the percent of volatiles was 3.93. The mean value of the dry density was 33.84 lbs/cu ft.

The same discrepancy between the billet density and the individual specimen mean density which has previously appeared in each billet appeared in Billet No. 12.

Billets 19, 22, and 26 were subjected to the whole billet tests and spot checking. No large variation from the previous billets was observed and the previous conclusion on variability were confirmed. The decision to perform only limited tests of these billets was supported by the lack of time remaining in the program to thoroughly test the billets and the request of NASA Ames to save most of the material for plasma arc testing.

Compressive Strength

Compression specimens were machined from Billets Nos. 2 and 8 in identical fashion to the density sampling. A total of 57 compression specimens, 0.505 inch diameter x 1/2 inch high, were fabricated from both billets. These specimens represented pairs of specimens from 3 height, 3 radial and 3 circumferential locations plus 3 height specimens at the central axis. A total of 18 compression specimens were machined from Billet 12. These specimens represented pairs of specimens from 3 height, 3 radial and 1 circumferential location. The specimens were 0.505 inch diameter by 1 inch high.

The summarized results of the compression testing are shown in Table 8.

Billet Number	Compressive Strength, psi		Number of Tests
	$\overline{X}$	S	
2	2435	±253	57
8	2575	±318	57
12	2820	±173	18

Table 8. Compressive strength of Langley billets.

Voids Content and Continuous Porosity by the Hughes Porosity Test

As previously described, (Appendix I) a method had been developed to impregnate ablator samples with epoxide resin and calculate the amount and type of voids. The final method using epoxide resin was selected after also evaluating silicone and polyester impregnants. The epoxide impregnation method is considered to be particularly suitable because the low impregnation pressure of 50 psi and the low curing temperature of $120^{\circ}F$ is not likely to cause degradation or major physical changes in the ablator specimens.

The results of porosity test on Billets Nos. 2 and 8 are shown in Table 9.

Specimen Number	Original Density	Continuous Voids as Percent of Total Void Volume	Continuous Voids as Percent of Total Volume of Sample	Discrete Voids as Percent of Total Volume (Calculated) of Sample
Billet No. 2				
A4R1D1-1B	0.541	68.9	38.1	17.2
A2R2D3-2B	0.552	67.7	34.8	17.6
A6R1D2-3B	0.572	65.7	34.6	18.1
A5R2D2-4B	0.551	68.2	37.1	17.3
		$\overline{X} = 67.6$	$\overline{X} = 36.2$	$\overline{X} = 17.6$
		$S = \pm1.4$	$S = \pm1.7$	$S = \pm0.4$
Billet No. 8				
A3-D2-R3	0.566	68.1	36.2	17.0
A4-D2-R3	0.556	68.9	37.3	16.8
A3-D2-R2	0.554	69.0	37.5	16.8
A4-D2-R2	0.554	70.5	38.2	16.0
A3-D2-R1	0.553	71.4	38.8	15.5
A4-D2-R1	0.550	71.2	38.8	15.7
A2-D2-R3	0.566	67.7	36.1	17.2
A5-D2-R3	0.567	66.1	35.1	18.0
A2-D2-R2	0.554	68.6	37.2	17.0
A5-D2-R2	0.554	70.3	38.1	16.1
A2-D2-R1	0.555	69.6	37.6	16.4
A5-D2-R1	0.562	71.0	38.0	15.5
A1-D2-R3	0.566	68.1	36.2	17.0
A6-D2-R3	0.570	65.5	34.6	18.3
A1-D2-R2	0.565	68.0	36.2	17.0
A6-D2-R2	0.573	67.8	35.7	16.9
A1-D2-R1	0.568	66.6	35.3	17.7
A6-D2-R1	0.571	67.0	35.2	17.3
		$\overline{X} = 68.6$	$\overline{X} = 36.8$	$\overline{X} = 16.8$
		$S = \pm1.8$	$S = \pm1.3$	$S = \pm0.8$

Table 9. Porosity of Langley billets by epoxide impregnation at 50 psi.

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The continuous porosity it should be noted was uniformly high and all porosity values between Billets 2 and 8 are similar.

Voids Content by Aminco Porosimeter

In order to determine the porosity of Billet No. 2, four specimens were submitted to Aminco for testing with the Winslow Porosimeter. These specimens were taken from the same areas in Billet No. 2 as the epoxy impregnated specimens reported in Table 9. Part of the data obtained were expressed in terms of volume percent of mercury penetrating the material and are presented in Table 10. Although the differences between specimens are small, an analysis of variance shows them to be significant.

As a sample of the type of data obtained, the curve for Specimen #1A-2A4R1D2 is shown in Figure 5. In addition, the pressures corresponding to the ultimate compressive strength of the material and to the first, second, and third quartiles of the crushing strength of the phenolic Microsphere filler are marked. The ultimate compressive strength pressure approximately coincides with the 90th percentile pressure of the Microsphere crushing strength.

Pres- sure PSI	Specimens				Extrap- olated Value
	1A-2A4R1D2	2A-2A2R2D2	3A-2A6R1D1	4A-2A5R2D3	
15	1.6	1.8	1.7	1.6	
30	24.6	24.9	22.5	24.4	
45	29.0	28.7	27.2	28.4	
60	30.6	30.5	29.2	30.0	
300	34.7	34.1	33.2	33.7	(35.2)
Epoxy Impreg. at 50	38.1	36.8	34.6	37.1	Mean Value (36.6)

Table 10. Porosity by Aminco porosimeter.
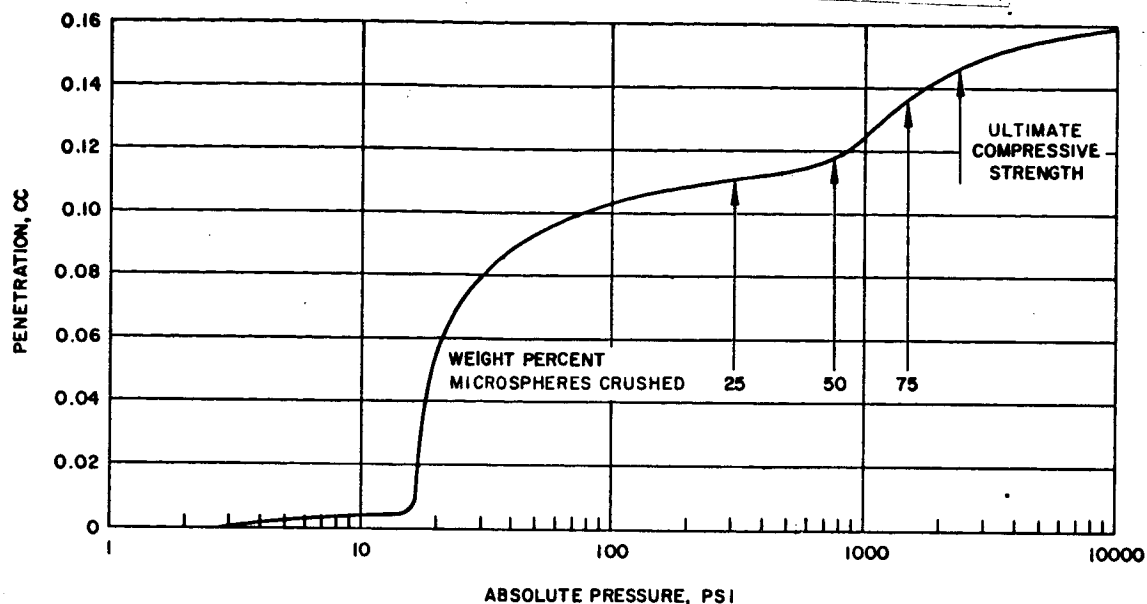
Figure 5. Porosity of Langley ablator billets by Aminco-Winslow porosimeter.

The two steps (zero slopes) are quite pronounced and could be interpreted as follows. At the low pressures the mercury is simply filling the continuous (or interconnected) voids until all are practically filled. Thereafter there is no change in volume with increases in pressure until the pressure is enough to collapse the walls enclosing the discrete voids which are thus added to the continuous voids. The second asymptote or step is obtained when all of this additional volume has been filled.

Figure 6 is a plot of the data of the same specimens (from Table 9) and is presented to show the portion of the curve in which essentially no crushing of Microspheres can take place. Use of a linear pressure scale in place of a log scale makes the zero slope portion more evident. Apparently the curve is that of a linearly transformed rectangular hyperbola with an asymptote corresponding approximately to an initial continuous void volume and an intercept corresponding to a pressure just sufficient to start penetration.
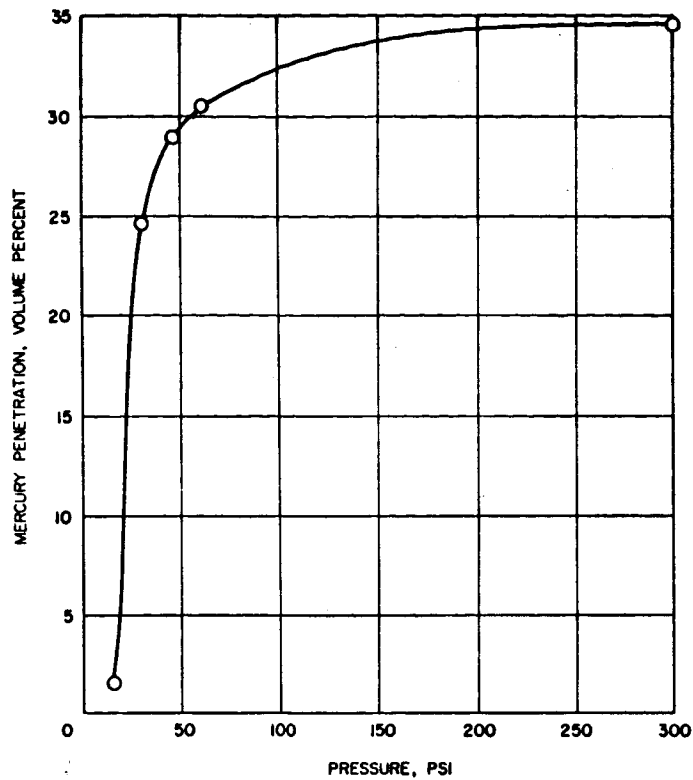
Figure 6. Penetration vs. pressure curve.

If the relationship

$$P = \frac{P_o V_\infty}{V_\infty - V}$$

(where P = pressure, V = volume, P_o = intercept, V_∞ = asymptote)
holds, then a plot of P_∞ vs P should yield a straight line.

Figure 6 shows that this is a satisfactory approximation. Least
squares estimates of the constants based on the data for all four speci-
mens of Billet No. 2 gave

$$P_o = 10.4 \text{ psi; and } V_\infty = 35.2\%$$

The asymptote value, 35.2% is close to the continuous void vol-
ume calculated from epoxy resin impregnation data, 36.6%. The sec-
ond asymptote value, 50.1%, might be expected to correspond to the
initial total void volume (assuming complete fracture and filling of

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microspheres). However this does not agree with the total void vol-
ume, 54.2%, calculated from the measured density.

2.3.3.2 Other Properties of Langley Ablator Billets

Photomicroscopy

As previously discussed no technique was found to section and
observe an untreated billet specimen without causing major damage to
the surface. However, it was found that specimens could be machined
and polished from epoxy impregnated billet specimens using standard
metallurgical techniques. A typical photomicrograph of a polished
impregnated billet surface is shown in Figure 4. The large irregu-
larly shaped areas of light hue are presumed to be nylon particles.
Rounded area with a sharply defined wall are microspheres. In all
observation made the great majority of microspheres were damaged
and filled with the impregnating resin. Also large void areas filled
with impregnating resin were observed as shown by scratch marks
from the polishing operation (runs diagonally from top right in Figure
4). The high degree of interconnected porosity revealed by the poros-
ity tests were therefore confirmed by direct observation, and the
assumption that microspheres were damaged by the molding process
was supported.

Examination of fractured surfaces of the Langley ablator with the
naked eye and by microscopy did however reveal a heterogeneous
structure containing many large nylon particles. A typical example is
shown in Figure 7.

Gas Transmission Tests

A simple gas transmission test was developed by passing air at
one atmosphere pressure through machined billet specimens and
measuring the gas flow with a gas burrette. The standard specimen
for this test had been a 3-inch diameter disc with a .250 inch thick-
ness. It was immediately discovered that air passed far too rapidly
through this thickness to obtain a reproducible and meaningful result.
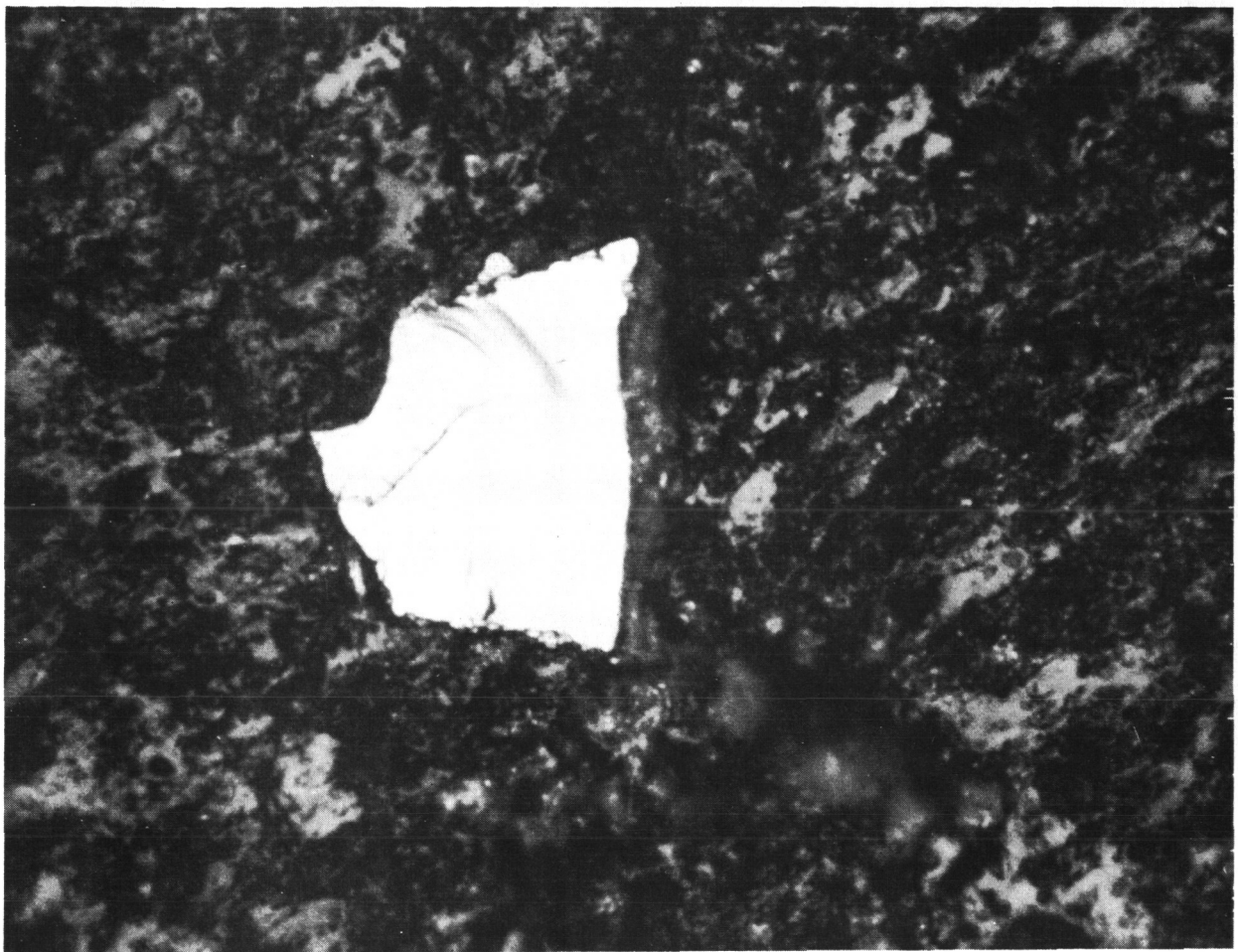
Figure 7. Photomicrograph (400X) of fractured surface of
Langley billet showing large nylon particle.

Later in the program a .750 inch diameter by 1.132 cylindrical speci-
men was utilized with air passing through in the axial direction. Even
with this specimen, air passed so readily through the Langley material
that flow was limited by the orifice size of the stopcock on the gas bur-
rette. Readings of 90 ml of air passed in 43 to 44 seconds were
obtained on all Langley specimens from all portions of the billet.
These results confirm the high porosity of this material although they
represent a figure lower than the gas transmission capability the
material.

Thermogravimetric Analysis

The presence of large nylon particles and the heterogeneity of the microstructure of the billet material presented difficulties in obtaining a reproducible small sample for TGA. It was therefore decided not to run TGA on the billet material and to concentrate TGA work on the raw materials.

Ash Content

The ash content from ignition of the billet material in air at 1000°F was determined to be similar to that of preproduction billets, that is approximately 1.5 - 1.3%. Little variation was found in the results and it was decided to discontinue this test as a quality control procedure.

Tensile Strength

Late in the program it was decided to compare the tensile strength of the Langley billet material with that of Hughes made nose cap material. Three tensile dog bone specimens were machined from the center of Billet #26 to the following dimensions: A 2" x 6" x 3/4" bar was necked down with a 3" radius cutter equally from both sides to form a 3/4 inch square cross section at the center of the tensile bar.

The results of these three tests were 288 psi, 330 psi, and 439 psi (avg 372 psi).

2.3.4 Summary of Langley Billet Characterization

The Langley ablators may be characterized as varying only to a small degree in bulk physical properties between billets and within billets. On the microscopic scale however they appear to be heterogeneous. The material is highly porous, and contains relatively large particles, crushed microspheres, and voids resulting in an uneven microstructure. The material is not a syntactic foam in the sense that the term syntactic means an ordered arrangement of voids. The low compressive and tensile strength combined with the high porosity of

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the material may be deleterious in high heat flux and high shear environments.

The variation within billets may best be summarized in terms of density; the most easily performed and precise quality control test used. The density tends to be high in the exterior layers of the part. Thus the density variation may be approximated as shown in Figure 8.

2.4 RAW MATERIALS CHARACTERIZATION

2.4.1 Phenolic Novolac

The characterization of any commercial phenolic novolac resin is complicated by the fact that the product is a mixture of the novolac resin and hexamethylene tetramine. The two materials are ground together into an extremely fine powder and it is extremely difficult to separate the two. Both the hexamethylene tetramine and the low molecular weight fraction of the novolac are water soluble. Any separation method involving increases in temperature tends to advance the resin (increase the molecular weight.) Attempts to separate the hexa from the base resin almost inevitably cause changes in the base polymer. One of the major efforts in characterizing the novolac was

AVERAGE PROPERTIES

	DENSITY lbs/ft^3	COMPRESSIVE STRENGTH psi	VOL % INTERCONNECTED POROSITY
CORE	33.4 ± .4	2000 ± 300	65 ± 10
SHELL	34.0 ± .6	2500 ± 500	50 ± 10
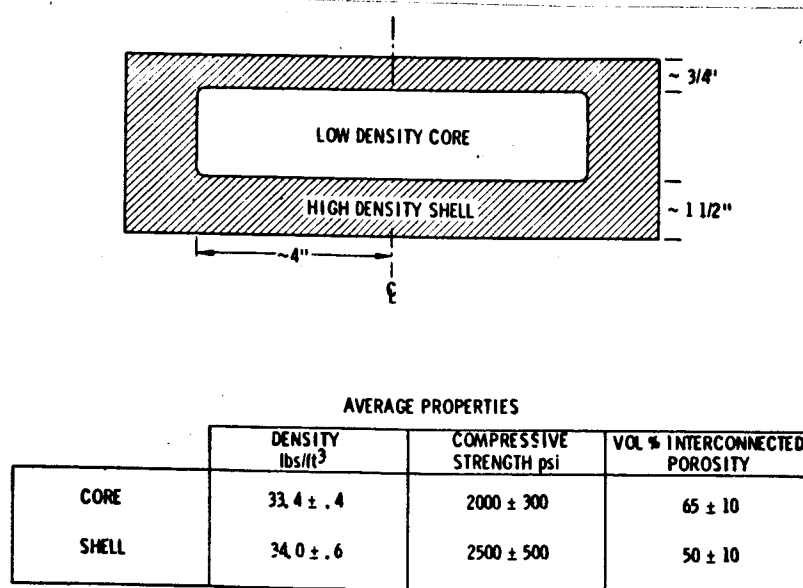
Figure 8. Schematic distribution of properties in Langley billet.

therefore to develop a method of removing the hexa with minimum change to the phenolic novolac.

Separation of Hexa

The method found most effective for removal of hexa from the commercial resin was washing several times in cool water accompanied by intensive mixing. It was found that five washings at a concentration of 4 pounds of resin to 10 gallons of pure water in a 20 gallon Hobart mixer effectively reduced the hexa content. The method of hexa removal is described in Appendix I. The removal of hexa was verified by a very low analysis for nitrogen on the washed product and an essentially infinite gel time. It was recognized that this treatment also removed water soluble phenols and dimers. A total of 14.7% loss of weight was obtained, consisting of approximately 9% hexa and approximately 6% low molecular weight phenols. The nitrogen content of the extracted material was 0.05% representing an efficient removal of hexa.

Apparent or bulk density measurements were attempted with powdered resin by weighing a container of resin having a fixed volume. Results are tabulated in Table 11.

The measurements indicate that a reproducible bulk density measurement may be difficult to achieve and that the density is affected by brief exposure to moisture.

Gel Point

Gel tests were run at $302^{\circ}F$ on a temperature controlled cure plate on phenolic novolac. Tests were run on samples of Batch No. C633A as received and after five water extractions. In addition, gel tests were run on six samples taken from various locations in a drum of Batch No. C1020A. Four gel tests were run on each sample. Wide variations within samples were obtained. Since it was felt that the large range in values could be due to moisture, one sample was dried 18 hours at $120^{\circ}F$ and the gel point redetermined. The drying

Volume of Measure 111 cc Container Tare Weight 17.6 gm		
Treatment	Net Wt-Gm	Density Gm/cc
Vibration Compacted	52.6	.474
Vibration Compacted	47.9	.432
Vibration Compacted	46.5	.419
Average		.442
No Compaction	40.6	.366
No Compaction	39.2	.353
No Compaction	37.9	.341
No Compaction	40.1	.361
No Compaction	39.7	.358
Average		.356
No Compaction - High Humidity	40.7	.367
	41.3	.372
	39.5	.356
Average		.365

Table 11.   Bulk density of commercial phenolic novolac.

procedure resulted in a much smaller range in test results.   The results are given in Table 12.

Gel tests at $300 \pm 2^{\circ}$F were repeated on six samples taken from various locations in a drum of phenolic novolac, Batch No. C1020A, after drying the samples for 18 hours at 120°F under vacuum.   The results obtained for samples XRCC and XRCO were very inconsistent. Gel determinations were then run on all six samples immediately after tumbling each sample vial.   These last gel times were relatively consistent.   It appears that some segregation of phenolic may take place on long standing.   The results are summarized in Table 13.

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Sample Description	Cure Time, Seconds			
	Test Number			
	1	2	3	4
Batch C633A, as received	178.6	180.0	153.1	106.8
Batch C633A, water extracted	458.2	468.2	259.8	295.5
Batch C1020A, Sample XRBO	110.3	110.6	110.1	118.0
Batch C1020A, Sample XRBC	106.3	130.7	103.5	147.4
Batch C1020A, Sample XRCO	107.3	113.8	115.2	94.4
Batch C1020A, Sample XRCC	100.0	117.2	105.2	118.0
Batch C1020A, Sample XRTO	89.3	91.0	92.5	103.1
Batch C1020A, Sample XRTC	99.3	103.6	96.6	97.5
Batch C1020A, Sample XRBC Dried 18 hrs at 120°F	103.8	104.9	99.8	98.2
(XRBO = bottom-outside, XRBC = bottom-center, XRCO = center-outside, XRCC = center-center, XRTO = top-outside, XRTC = top-center)				

Table 12. Gel point tests on commercial phenolic novolac.

These results emphasize the need for thorough mixing of the material before sampling for test. Evidently a large surface effect exists tending to increase the gel time. This effect is thought to be the loss of volatile phenols which exert a solvating effect during gel tests thereby increasing the speed of reaction.

Viscosity Number

The viscosity number of the uncured resin was determined according to Hughes Material Specification No. 16-1096. The method consists of measuring the viscosity and refractive index of a filtered solution of the resin in dimethyl formamide. The viscosity number is the diagonal band on a chart within which the intersection of the

Sample Designation	Sample Treatment	Gel Time, Seconds			
		Run Number			
		1	2	3	4
XRCC	Vacuum-dried, not tumbled. Taken from surface of material	273.8	318.5	339.1	292.6
XRCO		253.1	137.6	143.1	197.2
XRCC	Vacuum-dried, tumbled	122.3	123.2	123.7	120.0
XRCO		122.3	124.3	123.0	123.3
XRBC		125.2	125.7	124.3	123.9
XRBO		127.7	126.4	128.5	126.5
XRTC		128.0	135.2	135.1	130.7
XRTO		124.3	127.8	123.7	123.7

Table 13.   Gel point tests on vacuum-dried phenolic novolac.

refractive index and the viscosity lies.   The results of three determinations were virtually identical.   A viscosity number of 2.3 was obtained.

Extractables

The uncured phenolic resin was almost completely soluble in acetone and dimethylformamide.   An attempt was made to water-extract 500 gm of resin.   A total of five extractions with cold, distilled water left a residue of 426.5 gm (14.7 percent loss).

Volatiles

Volatiles determinations were made on six samples taken from various locations in a drum of Batch No. C1020A.   Determinations were made on two one-gram samples taken from each sample.   The volatiles were determined on the same material for two drying

conditions: 24 hours under vacuum at 120°F and 45 minutes at 300°F. The results in Table 14 show a pronounced effect due to location in the original drum and a large variation within samples in some cases.

Ash Content

The ash content of the dried samples remaining after the volatiles determinations described in the preceding section was determined by ignition to constant weight at 1300°F. The ash content values in Table 15 are based on the dried weight, not the original weight prior to the analysis for volatiles. The ash content is extremely low with no significant within drum variation.

Total Nitrogen

The total nitrogen was determined by the Dumas method on two samples taken from the top-center (XRTC) and the bottom-center (XRBC) of a drum of phenolic novolac, Batch No. C1020A. Two

Sample Designation	Location of Sample in Drum	Run No.	Volatiles, Weight-Percent		
			24 Hours 120°F (Vacuum)	45 Minutes at 300°F	Total
XRBO	Bottom, outside	1	1.12	0.46	1.58
		2	1.02	0.71	1.73
XRBC	Bottom, center	1	1.38	0.67	2.05
		2	1.24	0.63	1.87
XRCO	Center, outside	1	2.90	0.47	3.37
		2	3.98	0.47	4.45
XRCC	Center, center	1	1.30	0.61	1.91
		2	2.27	0.52	2.79
XRTO	Top, outside	1	4.45	0.47	4.92
		2	4.46	0.56	5.02
XRTC	Top, center	1	3.84	0.43	4.27
		2	4.54	0.46	5.00

Table 14. Volatiles in phenolic novolac, batch C1020A.

Sample Designation	Location of Sample in Drum	Run No.	Ash Content, Percent
XRBO	Bottom, outside	1 2	0.03 0.02
XRBC	Bottom, center	1 2	0.02 0.02
XRCO	Center, outside	1 2	0.02 0.03
XRCC	Center, center	1 2	0.02 0.02
XRTO	Top, outside	1 2	0.02 0.02
XRTC	Top, center	1 2	0.02 0.02

Table 15. Ash content of phenolic novolac, batch C1020A.

determinations were made on each sample. The results, given in Table 16 show no effect of sample location on total nitrogen content.

Moldability

Two one-inch diameter discs were molded from the unmodified resin, Batch No. C633A. The discs were cured for one hour at 300°F at a pressure of 200 psi. The material molded fairly well. However, a few small bubbles could be seen in both discs. Two small, bubble-free sections cut from disc were weighed in air and water. The specific gravity calculated from the results was 1.27.

Ash Content and Emission Spectra of Ash

The ash remaining after the ignition of Batch No. C633A was subjected to emission spectrographic analysis. Table 17 gives the semiquantitative results based on the ash weight and on the original weight of resin (ash content = 0.040%).

Sample Designation	Run No.	Total Nitrogen, Percent
XRBC	1	3.46
	2	3.50
XRTC	1	3.49
	2	3.52

Table 16. Total nitrogen content of phenolic novolac, batch C1020A.

Element	Percent (based) on Ash)	Percent (based on Unignited Weight)
Silicon	11.	0.0044
Iron	7.3	0.0029
Calcium	11.	0.0044
Aluminum	2.4	0.00096
Zinc	3.8	0.0015
Copper	2.4	0.00096
Magnesium	1.1	0.00044
Boron	0.52	0.00021
Manganese	0.11	0.000044
Lead	0.30	0.00012
Tin	0.65	0.00026
Chromium	0.66	0.00026
Nickel	1.2	0.00048
Silver	Trace	-
Titanium	0.30	0.00012
Zirconium	Trace	-

Table 17. Spectrographic analysis of ash of phenolic novolac.

Flow Characteristics of Catalyzed Resin

In order to obtain a simple quality control procedure for the resin and to gain a better understanding of its molding characteristics, it was decided to determine flow by conventional methods.

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It was found to be impossible to mold dense flow cups by ASTM method No. D 731-55T "Molding Index of Thermosetting Molding Powders." All the cups molded contained large bubbles and the flow times were erratic.

Flow was therefore checked with the Mesa Spiral Flow Mold; a method now being generally adopted by industry. In this method the molding material is transferred at the center of a heated spiral mold. The Archimedean spiral cavity has a pitch of 1/2 inch and the channel is 0.250 wide, 0.082 inch deep, and 48 inches long. Flow is measured in inches of the spiral filled by the material under controlled conditions of pressure, temperature, and charge weight (see Figure 9). The procedure is described in Appendix III.

Reproducible flow measurements were obtained with the spiral flow mold which should be suitable for specification requirements. Preliminary results are tabulated in Table 18.

Load on 2" Dia Ram Lbs	Mold Temp. °F	Charge Wt gm	Length of Flow-Inches (Solid Molding)	Length of Flow-Inches Total
10,000	300	25	2.3	+48
10,000	300	35	48+	+48
2,500	300	35	2.7	2.85
2,500	300	35	3.2	3.45
2,500	300	35	2.5	2.85
2,500	325	35	1.9	2.5
2,500	325	35	2.1	2.2
2,500	350	35	1.0	2.1
2,500	350	35	1.1	2.4
2,500	250	35	-0-	-0-
2,500	250	35	-0-	-0-

Table 18. Spiral flow of commercial phenolic novolac (as received).
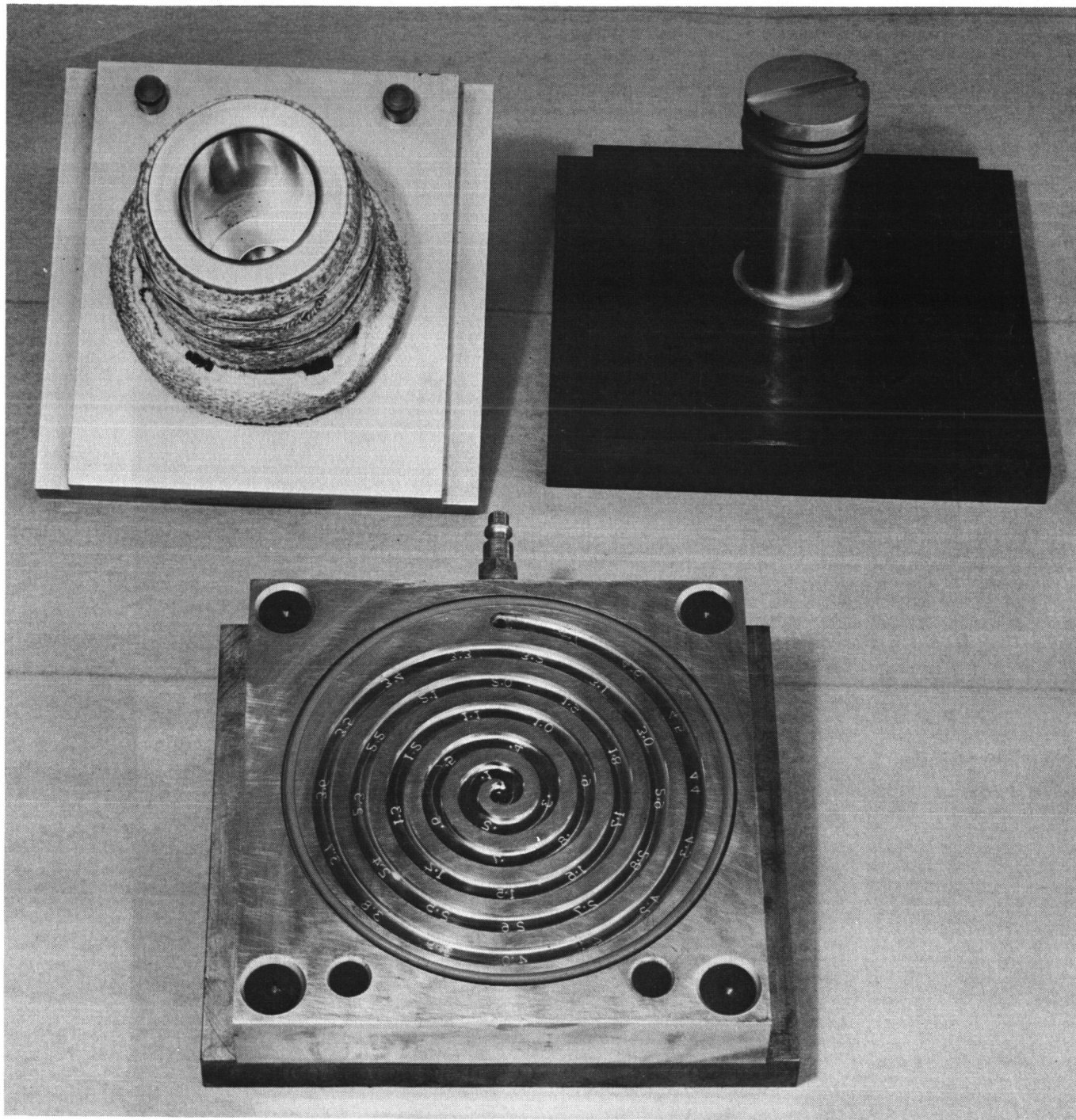
Figure 9.   Mesa spiral flow mold.

Variability of Hot Plate Cures of Novolac Specimens from a Drum

An experiment was performed to determine whether specimens taken from different locations in a drum of phenolic novolac would be variable in hot plate cure. Specimens were taken from six different locations in the drum, viz.,

> Axis - top
> Axis - center
> Axis - bottom
> Wall surface - top
> Wall surface - center
> Wall surface - bottom

After tumbling each specimen four hot plate cure tests at $302^{\circ}F$ were performed on it. Results are shown in Figure 10.
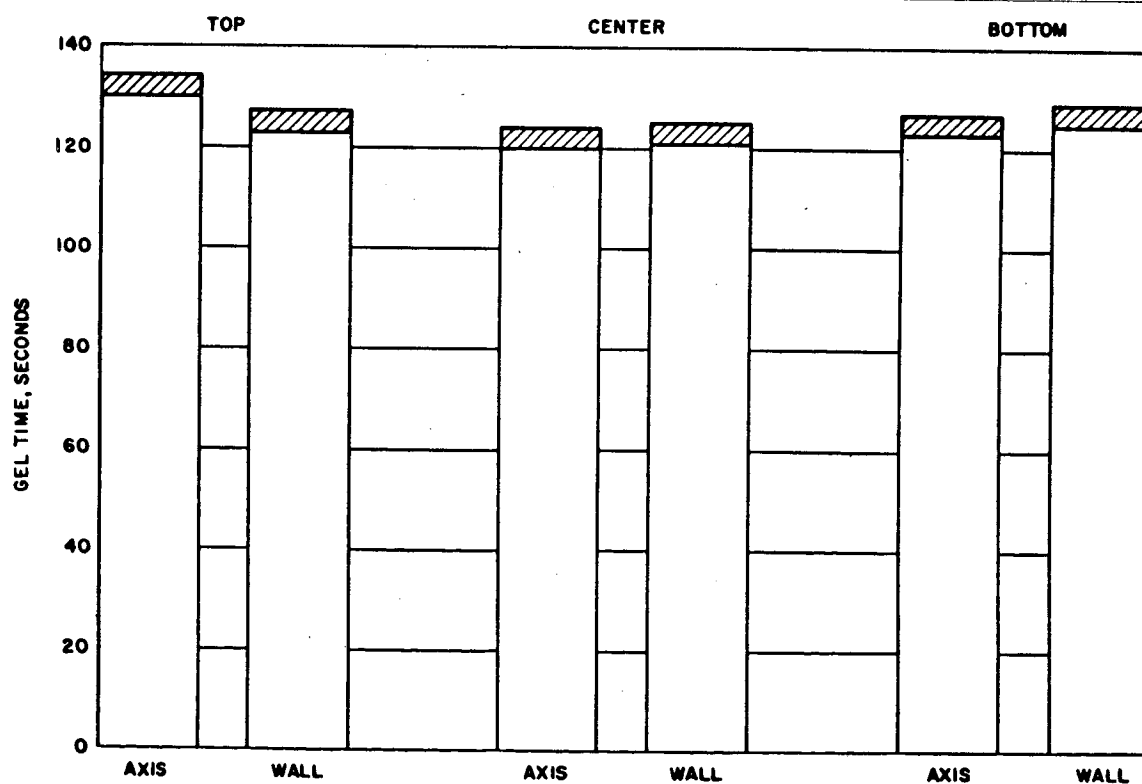
Figure 10. Cure speed of novolac taken from various positions in the drum.

A Bartlett's test showed that there was no significant difference between error variances and hence pooling could be done.

An analysis of variance revealed that there was no significant radial effect (from axis to wall). However the axial effect (top to bottom) and interaction were highly significant at levels of $P < .001$.

Ninety-five percent confidence intervals of means were calculated and are shown plotted in the figure. This illustrates the significant effects. The axial effect is due to the slightly higher cure speed of specimens taken from the center of the drum.

The interaction is attributable to the slow cure of the specimen taken from the axis-top location.

It is possible that these differences reflect differences in hexa content. The material is a blend of novolac and hexa and the possibility of some segregation in transit exists. However, the differences are probably not of sufficient magnitude to cause difficulties in production.

Melting Point of Extracted Phenolic Novolac

The melting point of vacuum-dried, freshly tumbled, water-extracted phenolic novolac (gel time = 150 minutes) was determined and compared with that of two Hughes-synthesized novolacs, HFN-2 and LFN-3 (described later). The melting points obtained are shown in Table 19.

Fractionation of Phenolic Novolac

Water-extracted phenolic novolac (gelation time, 150 minutes) was fractionated by precipitation with water from an acetone solution.

Resin	Melting Point, $^\circ$C Av.
Phenolic Novolac, Water Extracted	114
HFN-2	89
LFN-3	79

Table 19. Melting point of novolacs.

One hundred (100) gm of resin was dissolved in 900 gm of acetone. Water (approximately 250 ml) was added slowly until the solution was faintly turbid, then a small quantity of acetone was added to remove the turbidity. Two large fractions (49.98 and 45.59%) were obtained by successive additions of two 100 ml quantities of water. The fractions were separated by the use of a centrifuge. Each fraction was vacuum-dried to a hard cake, ground to a fine powder and vacuum-dried for 18 to 36 hours. The small fraction remaining was not recovered. The fractions were submitted for determination of molecular weight.

Thermogravimetric Analysis

TGA curves were run on the commercial novolac and on a Hughes synthesized novolac (designated LFN-1H) at both Hughes and on standard equipment at Aminco.

Since TGA data of both Aminco and Hughes on the commercial phenolic novolac and on the Hughes low factor novolac were available it was decided to compare laboratories.

An analysis of variance showed that laboratories were highly significant as a primary factor and as interactions with resins and with temperatures (P equal .001 in all cases). The first arose from the tendency of the Hughes weights to be rather consistently lower than the Aminco values at corresponding temperatures. The laboratory resin interaction simply means that Aminco discriminated between resins more clearly than Hughes. The laboratory-temperature interaction can be interpreted as a reflection of the tendency of the Aminco weights to approach an asymptote at high temperature contrary to the case of the Hughes data.

Figures 11, 12, and 13 are plots of the data analyzed and show the effects.

41
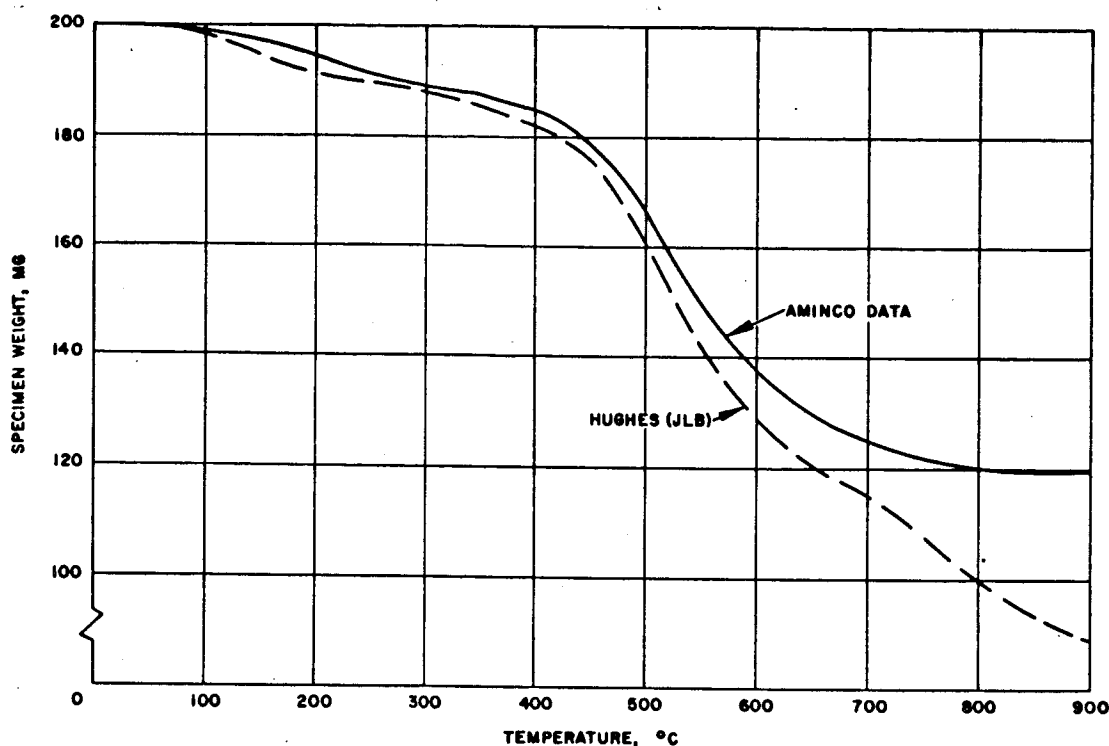
Figure 11. TGA curves of sample XR1-commercial phenolic novolac.

Effect of Heating on TGA Curves

TGA data from Aminco obtained on two specimens of commercial phenolic novolac were available for analysis of the effect of using different heating rates.

Inspection of the smoothed curves reveals that the lower heating rate (180°C/hr) results in the high temperature flattening occurring at a higher residual weight level than that of the higher heating rate (360°C/hr). It was decided to establish whether or not this difference was attributable to random error.

The numerical values were selected for analysis following the procedure described in last month's report.

The analysis showed that the only significant factor, aside from temperature of course, was the temperature-heating rate interaction (P = .01). Thus the difference in high temperature flattening levels was real.

42
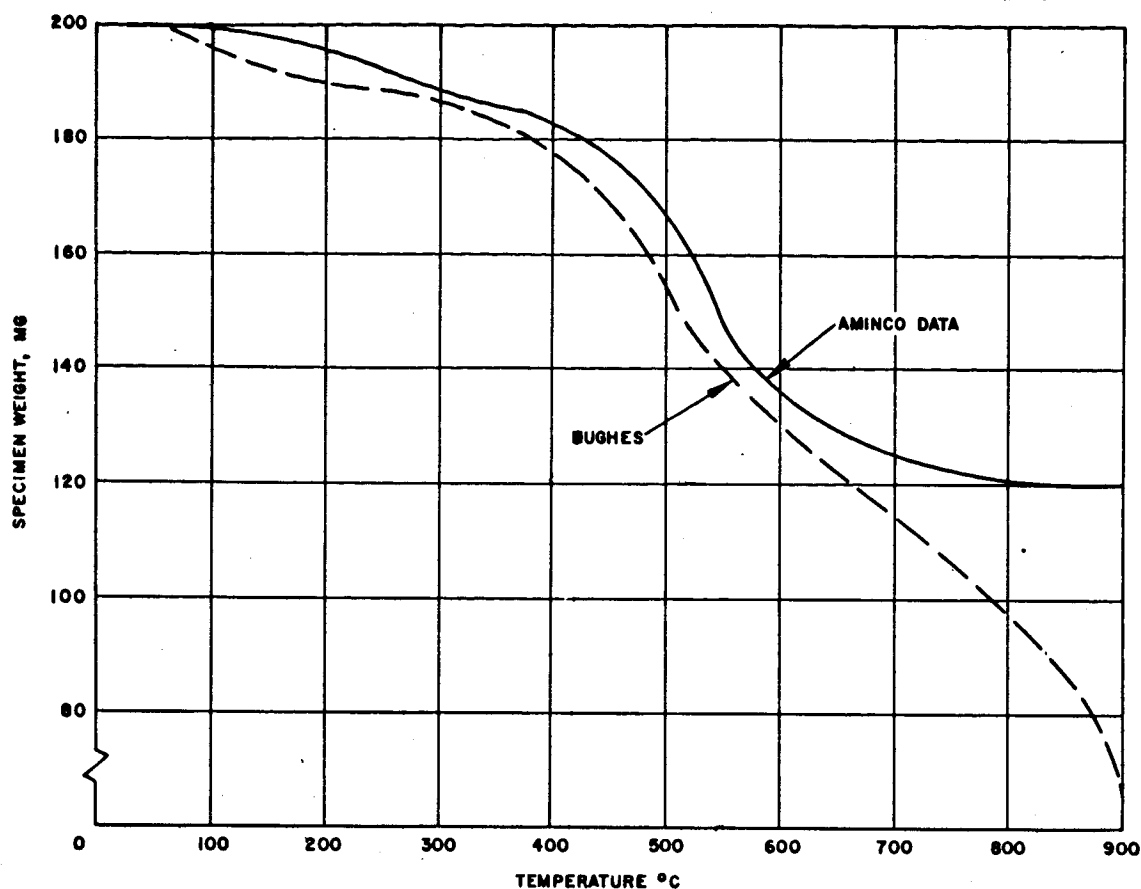
Figure 12. TGA of sample XR3 — commercial phenolic novolac.

The effect is illustrated in Figure 14. These curves are smoothed plots of the 18 selected values. Similar curves of the Hughes low factor novolac are shown in Figure 15.

It is interesting to note that the heating rate effect is reflected to a rather minor degree in the two calculated integral procedural decomposition temperatures as shown in Table 20.

The reversal in rank from one ipdt to another calls for some comment.

The lower heating rate is associated with a higher final weight. This can be construed as a higher degree of "refractoriness" which, according to Doyle (Reference 7) (WADD-TR 60-283), is discounted in the T_{A*K*} calculation. Possibly this property has been over-discounted.

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SPECIMEN WEIGHT, MG

HUGHES

AMINCO DATA
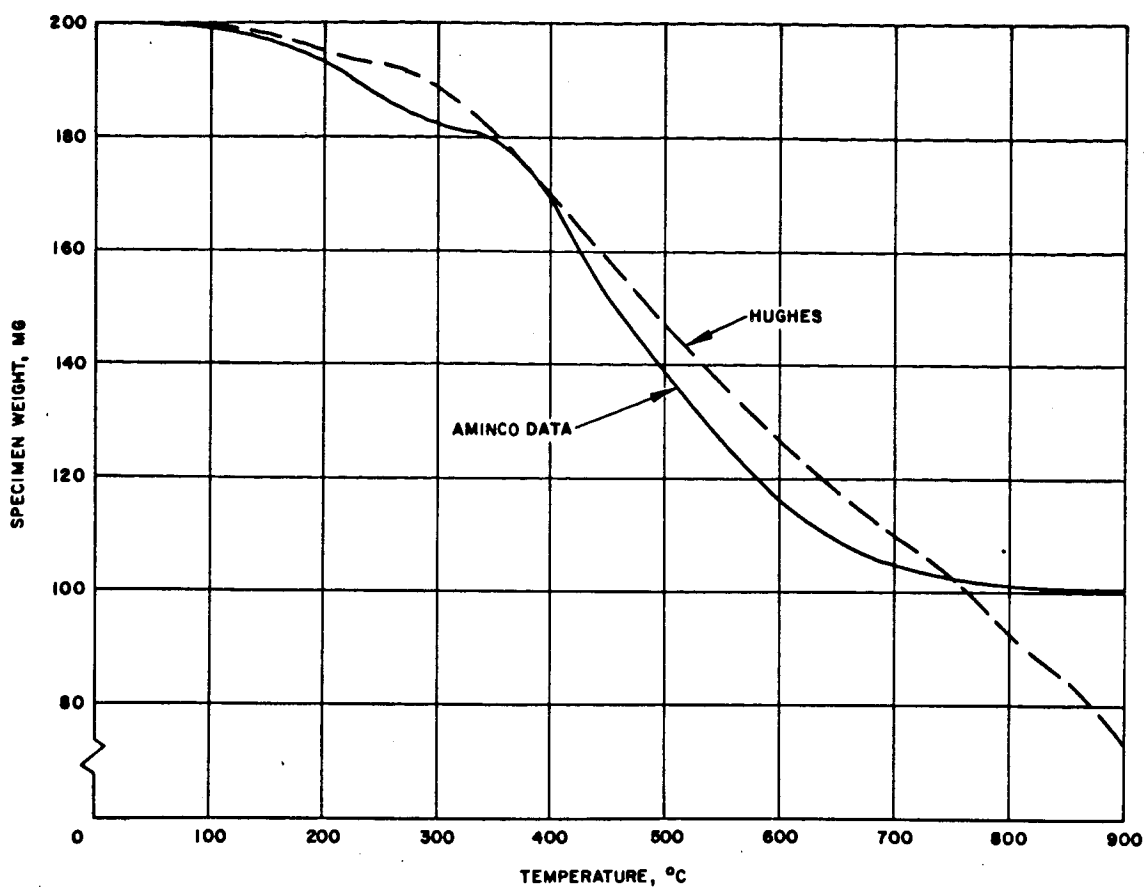
TEMPERATURE, °C

Figure 13. TGA curves of LFN-1 (H), Hughes synthesized novolac.

Heating Rate °C 1 hr	T_{A*} °C	T_{A*K*} °C
180	741	392
360	737	402
(Each calculated temperature is a mean of two values)		

Table 20. Effect of heating rate on TGA.

Considering the small effect of such a large difference in heating rates it is obvious that test results will be relatively insensitive to the minor fluctuations in heating rate to be expected in practice. (Some fluctuation might be anticipated from one test to another due to differences in ambient temperature or changes in air currents.)
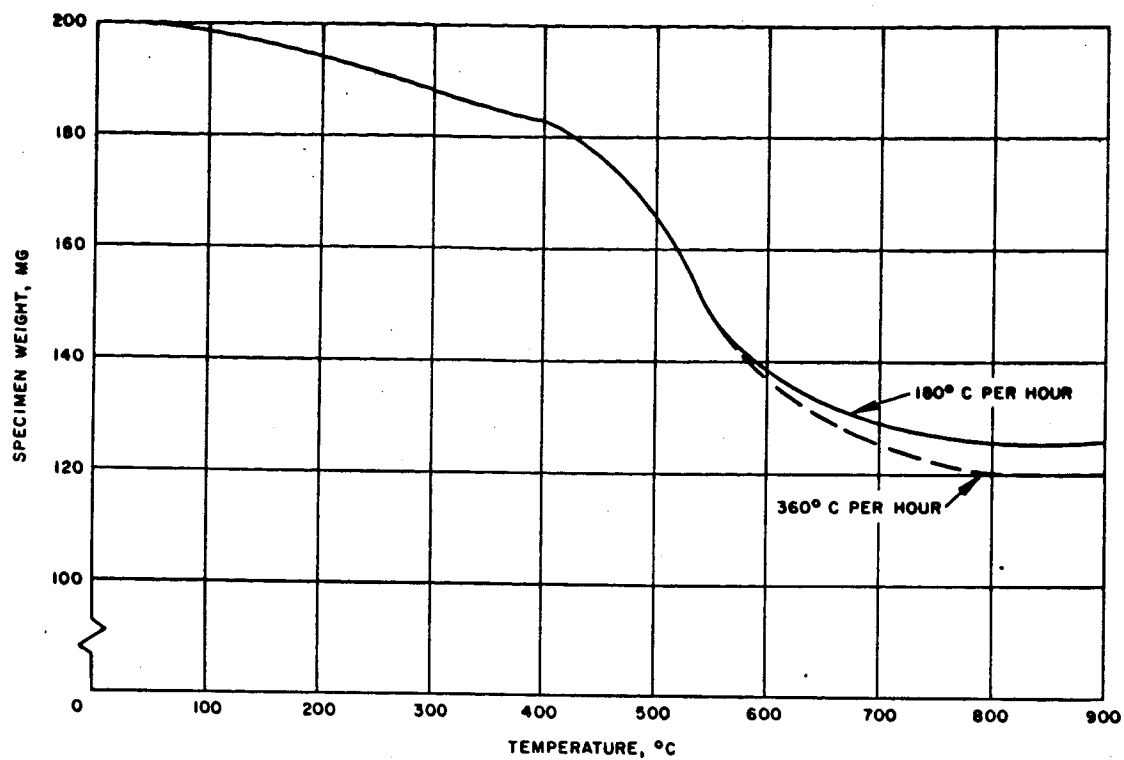
Figure 14. TGA curves of commercial novolac at two heating rates.
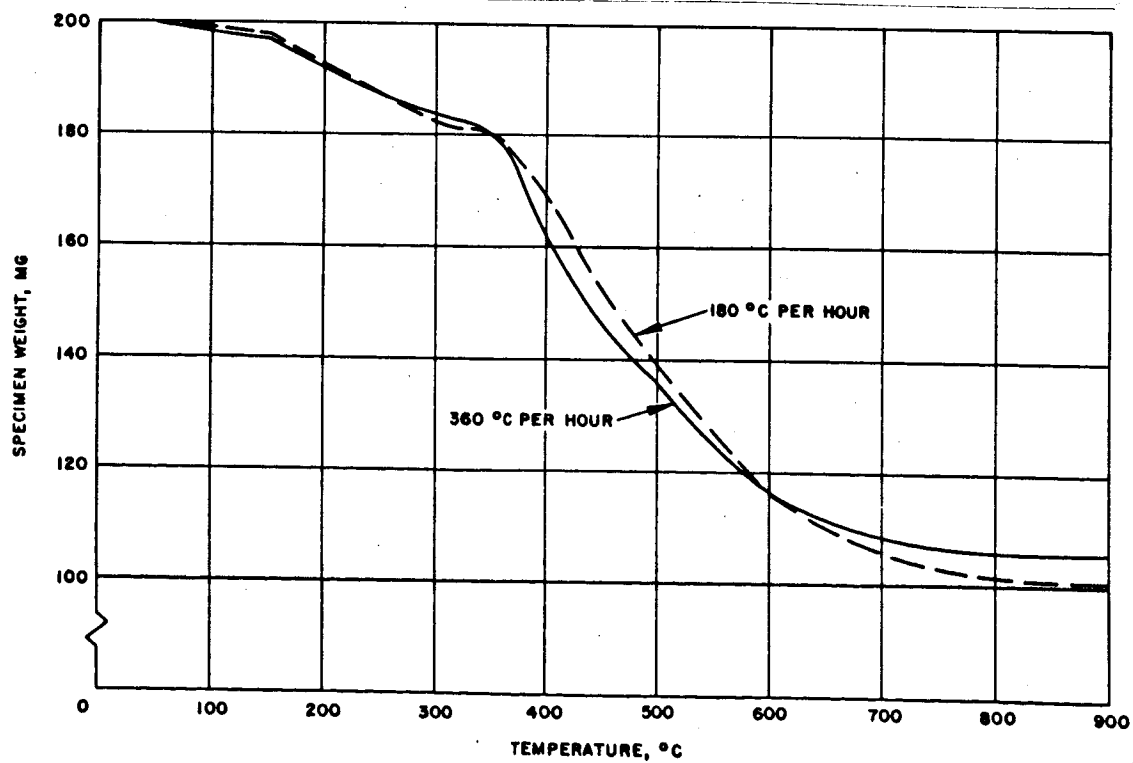
Figure 15. TGA curves of LFN-1, (Hughes) at two heating rates.

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IR Absorption Spectrophotometry

IR spectrophotometric scans on the commercial novolac were run with a Beckman Mod. IR-5 instrument, and with a Perkin-Elmer Model 12, in an effort to characterize the novolac.

The spectra of several samples of novolac were compared with those of two similar commercial Novolacs. The commercial novolac samples were taken up in dry acetone and the resulting solution was placed on Na Cl windows and evaporated. A strong absorption at 9.8 microns was observed in the spectra of the Langley novolac but no absorption at this wavelength was found in the spectra of the other two tested. Since in an acid-catalyzed phenol-formaldehyde condensation few methylol groups would be formed, the 9.8 micron band is attributed to the hexamethylene tetramine (Hexa) in the Langley novolac. The carbonyl content of the Langley novolac, based on absorption at 6.22 microns and the apparent advancement of cure, as indicated by the relative intensities of the 12.2 and 13.2 micron bands[1], was very nearly the same as the other resins. The Langley novolac resin contains some free phenol as indicated by absorption at 14.4 microns as well as by hydroxyl stretching absorption.

No quantitative measurements of carbonyl concentration or percentage of 2/21 methylene linkages in the Novolac were made pending choice of an optimum procedure for examining samples. It was determined that quantitative IR measurements can best be made on novolac samples in acetone solution at a 4-5% solids level in accordance with the method of Reed and Favero (Ref. 8).

Molecular Weight Determination

The molecular weight of water extracted commercial novolac was determined by ebulliometric methods using dioxane as solvent. The number average molecular weight extrapolated to zero concentration of washed and dried commercial novolac was 1337. Correcting this value for the approximate 5% of low molecular weight products removed during the extraction of hexa, provides a molecular weight of

approximately 800. A description of the procedure for determining molecular weight is found in Appendix III, Item 3.

Summary of Commercial Phenolic Novolac

Characterization

The commercial resin used in the Langley formulation is a typical phenolic novolac having a fast cure rate and containing a very low percentage of foreign impurities. The data developed on this material is summarized in Table 21.

The investigation revealed that large differences in flow time and volatiles content occur within a drum of the material and therefore it

Property	Value
Mesh Size	All passes 325 Mesh
Bulk Density	0.35 gm/cc
Molded Density	1.27 gm/cc
Gel Time at 300°F	99-125 Sec.
Volatile Content (45 min. @ 300°F)	~5%
Hexamethylene Tetramine Content	9%
Total Nitrogen	35%
Water Extractables	14.7%
Water Soluble Low Molecular Wt. Products	5 - 6%
Melting Point (water extracted Mat'l)	114°C
Number Average Molecular Weight	~800
Viscosity Index	2.3
Flow (Mesa Spiral) 2500 lbs, press load at 300°F	2.8-3.5 inches

Table 21. Summary of properties of commercial phenolic novolac used in the Langley ablator.

should be thoroughly mixed before use. The question of batch to batch variability remains unanswered except for the limited evidence obtained in comparing gel times of Batch No. C633A and C1020A. The material tested was of high purity in terms of ash content. The high percentage of water soluble organic material may be a source of variability in future batches because it indicates incomplete reaction and insufficient stripping of the finished product. These are indications however that the presence of the low molecular weight materials increases flow of the resin and is therefore advantageous in processing.

2.4.2 Phenolic Microspheres

In characterizing the phenolic microspheres it was considered necessary to obtain an understanding of the particle size distribution and the damaging effects of pressure. Considerable work was performed in developing methods for determining true density and the percentage of fractured microspheres under vacuum pressure conditions. It is believed that the information developed will be helpful in the understanding of the role of microspheres in syntactic foams and the development of optimum processes.

Apparent or Bulk Density

Using the procedure described for bulk density measurements of phenolic novolac, measurements were made on as-received microspheres and on microspheres subjected to 100% relative humidity for 24 hours. Table 22 summarizes the data.

Volatiles

Volatiles determinations were run on six samples taken from various locations in a drum of phenolic microspheres, Batch No. C505. Two determinations were run on each sample. The weight loss was recorded after 30 minutes at 300°F. An additional 15 minutes resulted in no further weight loss. Table 23 summarizes the data.

Volume of Measure 111 cc Container Tare Weight 17.6 gm		
Treatment	Net wt-Gm	Density Gm/cc
Vibration Compacted (test abandoned due to extreme variation of bulk)	11.7	.105
No Compaction	9.6	.086
No Compaction	9.0	.081
No Compaction	9.2	.083
No Compaction	9.5	.086
No Compaction	9.2	.083
Average		.084
No Compaction (High humidity)	11.2	.101
	10.6	.095
	11.3	.102
Average		.099

Table 22. Bulk density of phenolic microspheres.

Sample Designation	Location of Sample In Drum	Run No.	Volatiles (45 Min. at 300°F) Percent
XBBO	Bottom, outside	1 2	4.07 3.50
XBBC	Bottom, center	1 2	5.07 4.08
XBCO	Center, outside	1 2	3.64 3.75
XBCC	Center, center	1 2	3.56 3.60
XBTO	Top, outside	1 2	3.50 3.58
XBTC	Top, center	1 2	3.82 3.90

Table 23. Volatile content of phenolic microspheres.

Ash Content and Emission Spectrographic Analysis

The ash content of the dried samples from the volatiles determinations was determined by ignition to constant weight at 1300°F. The values in Table 24 are based on the dried weights after removal of volatiles.

The ash remaining (5.38%) after the ignition of sample XBCO from a drum of phenolic microspheres was subjected to emission spectrographic analysis. Table 25 gives the semiquantitative results based on the ash weight and on the weight before ignition.

Sieve Analysis

The particle size and distribution of phenolic microspheres was completed for twenty-one samples of approximately 15 grams each. Three samples were run from each of six locations in the drum and three samples from the complete mixture of the drum. The specific sampling locations were at the top, center and bottom of the drum with one set along an outside edge and one set along the center axis. Six

Sample Designation	Location of Sample in Drum	Run No.	Ash Content, Percent
XBBO	Bottom, outside	1 2	4.98 5.45
XBBC	Bottom, center	1 2	4.99 4.86
XBCO	Center, outside	1 2	5.38 5.19
XBCC	Center, center	1 2	5.09 4.68
XBTO	Top, outside	1 2	5.45 5.31
XBTC	Top, center	1 2	5.02 5.02

Table 24. Ash content of phenolic microspheres.

Element	Percent (based on ash)	Percent (based on unignited weight)
Sodium	41.	2.2
Potassium	2.2	0.12
Calcium	0.19	0.010
Silicon	0.44	0.024
Magnesium	0.066	0.0036
Aluminum	0.063	0.0034
Boron	0.016	0.0008
Manganese	0.0011	0.00006
Lithium	0.0091	0.00049
Copper	0.031	0.0016
Silver	0.0079	0.00042
Nickel	Trace	-
Strontium	Trace	-
Chromium	0.00082	0.000044

Table 25. Constituents of ash from phenolic microspheres.

sieves were used. The sieve numbers and their corresponding maximum hole sizes are as follows: 50 - 0.0116", 80 - 0.0070", 120 - 0.0049", 170 - 0.0035", 230 - 0.0024" and 325 - 0.0017". The lower pan caught all particles smaller than 0.0017". The results of the sieving are shown in Table 26.

Particle Size and Distribution

The measurement of particle size and distribution was determined by sieve analysis and photomicrography.

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	Percentages on Each Sieve					
Sieve No.	Top Center			Top Outside		
	1	2	3	1	2	3
50	0.42	0.40	0.41	0.39	0.39	0.40
80	6.54	7.79	5.55	4.09	4.24	3.91
120	34.75	35.56	35.08	34.89	32.20	30.99
170	30.08	29.80	30.35	33.32	33.43	33.52
230	17.94	15.73	16.69	16.78	19.18	18.72
325	8.29	8.00	8.85	7.96	8.06	9.43
Pan	1.98	2.72	3.06	2.57	2.49	3.04
	Center Center			Center Outside		
50	0.39	0.35	0.31	0.38	0.46	0.44
80	3.88	4.06	3.72	4.31	3.80	4.02
120	30.44	30.69	28.02	32.33	28.44	28.99
170	34.06	34.39	33.58	33.50	34.69	33.92
230	17.58	17.20	19.65	18.14	19.91	19.28
325	10.64	9.82	10.98	8.79	9.72	10.34
Pan	3.00	3.49	3.75	2.55	2.97	3.00
	Bottom Center			Bottom Outside		
50	0.57	0.56	0.40	0.56	0.64	0.52
80	4.15	4.24	3.64	4.21	4.12	3.96
120	31.92	32.28	27.28	34.03	30.04	30.01
170	32.62	32.85	34.57	31.73	33.60	33.11
230	18.24	17.37	19.44	17.17	18.95	18.53
325	9.75	9.74	10.49	9.93	9.72	10.75
Pan	2.76	2.95	4.19	2.38	2.92	3.11
	Drum Mixture					
50	0.31	0.36	0.37			
80	4.59	4.42	4.45			

Table 26. Results of sieving phenolic microspheres.

Percentages on Each Sieve				
Sieve No.	Drum Mixture (continued)			
	1	2	3	
120	31.71	30.27	32.47	
170	32.51	33.31	33.10	
230	17.80	18.45	17.87	
325	9.30	9.46	9.25	
Pan	3.79	3.74	2.49	

Table 26 (continued). Results of sieving phenolic microspheres.

Sieve analysis was performed using 25 gm samples and the following sieve numbers as shown in Table 27.

Samples were selected from various locations within the drum to study the effects of packing and handling. Photomicrograph at 50X and 100X were taken by taping microspheres to pressure sensitive tape. Figure 16 illustrates a typical variation in size of microspheres.

For the sieve analysis one quart of microspheres was taken at each of six points within a drum. From each quart three specimens were drawn and tested for particle size distribution. The question to be resolved was whether the 18 distributions could be considered uniform or biased with respect to location in the drum.

Inspection of the data indicated that the distributions were apparently different. Rather than compare all 18 distributions it was decided first to compare the two extremes by a graphical method. Cumulative distributions of the two extremes were calculated and plotted on probability graph paper, (see Figure 17). This figure shows that, with the exception of the data of the coarsest screen, all of the points of a given distribution fall quite close to a straight line. Note, however, that the points of the two distributions do not fall on the same straight line. Therefore each set of data can be approximated by a different normal distribution except for the previously noted values.

Sieve No.	Opening, Ins.	Opening, Microns
50	0.0116	294
80	0.0070	177
120	0.0049	125
170	0.0035	88
230	0.0024	62
325	0.0017	44

Table 27. Sieve numbers and openings.
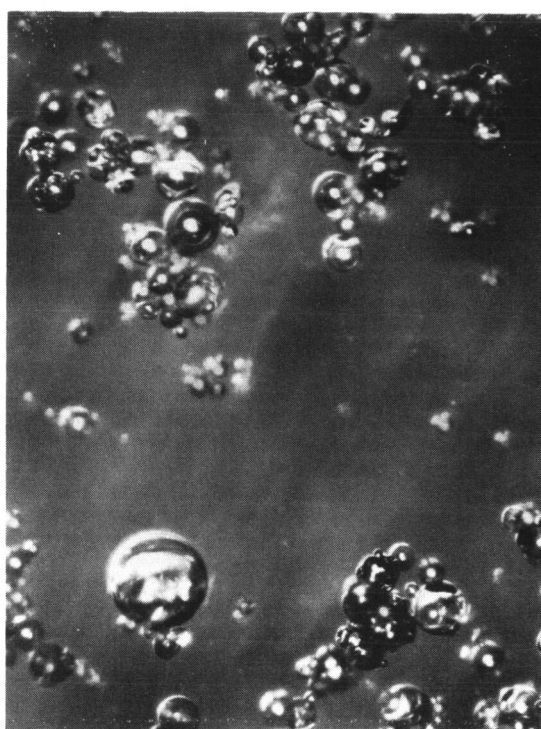
Figure 16. Photomicrograph of phenolic
microspheres at 100X.
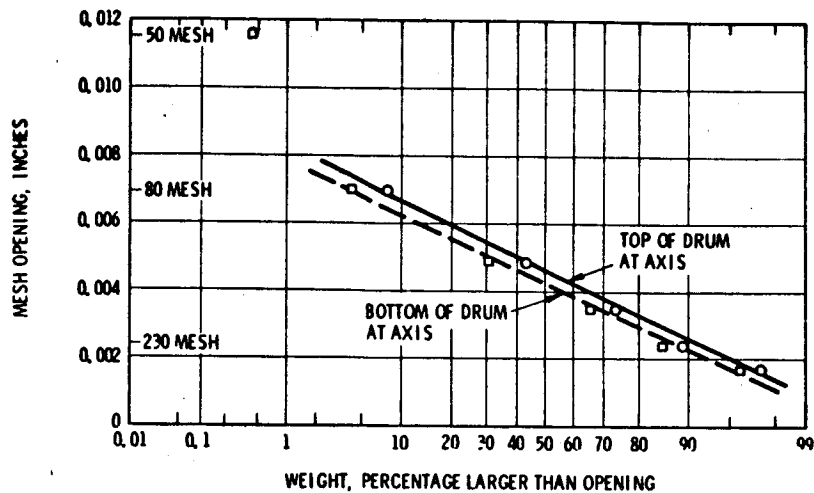
Figure 17.   Distribution of particle sizes of phenolic microspheres.

At this point it might be well to digress and consider some addi-
tional information that seems to throw light on the apparently anoma-
lous values.   Recently some microscopic examinations of this coarse
fraction have been made.   These examinations revealed that this frac-
tion did not consist of only large microspheres.   On the contrary it
also contained irregular chips of phenolic resin and asymmetric
agglomerates of fused microspheres.   (Figure 18) Thus this fraction
can be considered as having been drawn from a different universe than
the other fractions and should not be included with them.   In short this
point should not be included with the others in the figure.

Of course it should be pointed out that this fraction is so small
that it is not likely to give rise to any problems despite the heteroge-
neity of the shapes of its particles.

Returning to the probability plots it is quite evident that the
means of the two distributions are different but that the standard devi-
ations are approximately equal.   (Note the parallelism of the lines.)
Since these two lines represent the extremes, the remaining 16 distri-
butions will fall in the band between them.   Considering the narrow-
ness of the band one can say that from a practical standpoint there
does not appear to be any important difference between distributions.

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Figure 18.   Photomicrograph (400X) of phenolic
microsphere agglomerate.

However since there seemed to be a difference between the
means of the extremes it was decided to perform a statistical analysis
to determine whether there was any variability from specimen to spec-
imen and, if so, its association with location in the drum.   For this
analysis it was decided to use the medians of the 18 distributions as
variables.   (See Table 28.)

An analysis of variance showed that the only significant factor (at
the P equal .01 level) was the axial distance from top to bottom.
Neither the radial distance nor the interaction was significant.   Thus
there appears to be some tendency to stratification in horizontal planes

	Along Axis	Along Wall
Top of Drum	.00451	.00445
Top of Drum	.00461	.00435
Top of Drum	.00449	.00429
Center of Drum	.00427	.00436
Center of Drum	.00429	.00420
Center of Drum	.00415	.00422
Bottom of Drum	.00433	.00440
Bottom of Drum	.00435	.00427
Bottom of Drum	.00414	.00424

Table 28. Median mesh sizes of phenolic microspheres.

but only random variability in a given plane. The effect is shown below of the 95% confidence limits of the means with respect to the significant factor.

Drum Location	95% Confidence Limits	
	Low	High
Top	.00437	.00453
Center	.00417	.00432
Bottom	.00421	.00436

Center and bottom are indistinguishable from one another but the top tends to be higher. However the differences are so small that in sampling this drum for quality control testing it is unnecessary to maintain the axial and radial distinctions used in this work. In other words, this work leads to the conclusion that a sample drawn from any part of the drum can be considered as representative of its contents.

Since only one drum was involved in this program the results cannot be generalized to apply to all drums without additional work.

The sieve analysis results are significant however in adding to our understanding of the physical nature of the microspheres and will aid in producing a characterized and uniform material. It is obvious that all fractions not passing a 80 mesh opening sieve should be discarded in formulating a controlled syntactic foam.

True Density of Phenolic Microspheres

The true density of phenolic microspheres was determined by the use of the special apparatus shown in Figure 19. The method consists of displacing a known weight of liquid of known density in a modified pycnometer. Due to the low density of the microspheres, a pycnometer with a sintered glass septum was used. The displacement liquid used was toluene (density at $77^\circ F$ = 0.866 gm/cc) modified by the addition of a few drops of wetting agent. Duplicate tests were run on samples taken from the top and the bottom of the shipping drum. The results show a significantly large difference in true density as measured by this method. (See Table 29.)

Description	Location Within Drum			
	Top		Bottom	
	Run #1	Run #2	Run #1	Run #2
Weight of Microspheres, gm	6.292	6.695	6.846	6.0341
Weight of Toluene, no Microspheres, gm	265.042			
Weight of Toluene, Microspheres present, gm	240.079	238.968	240.779	243.506
Volume of Microspheres (decrease in volume of Toluene), cc	28.825	30.108	27.384	24.868
Density of Microspheres, lb/cu ft	13.62	13.88	15.60	15.14

Table 29. True density of microspheres.
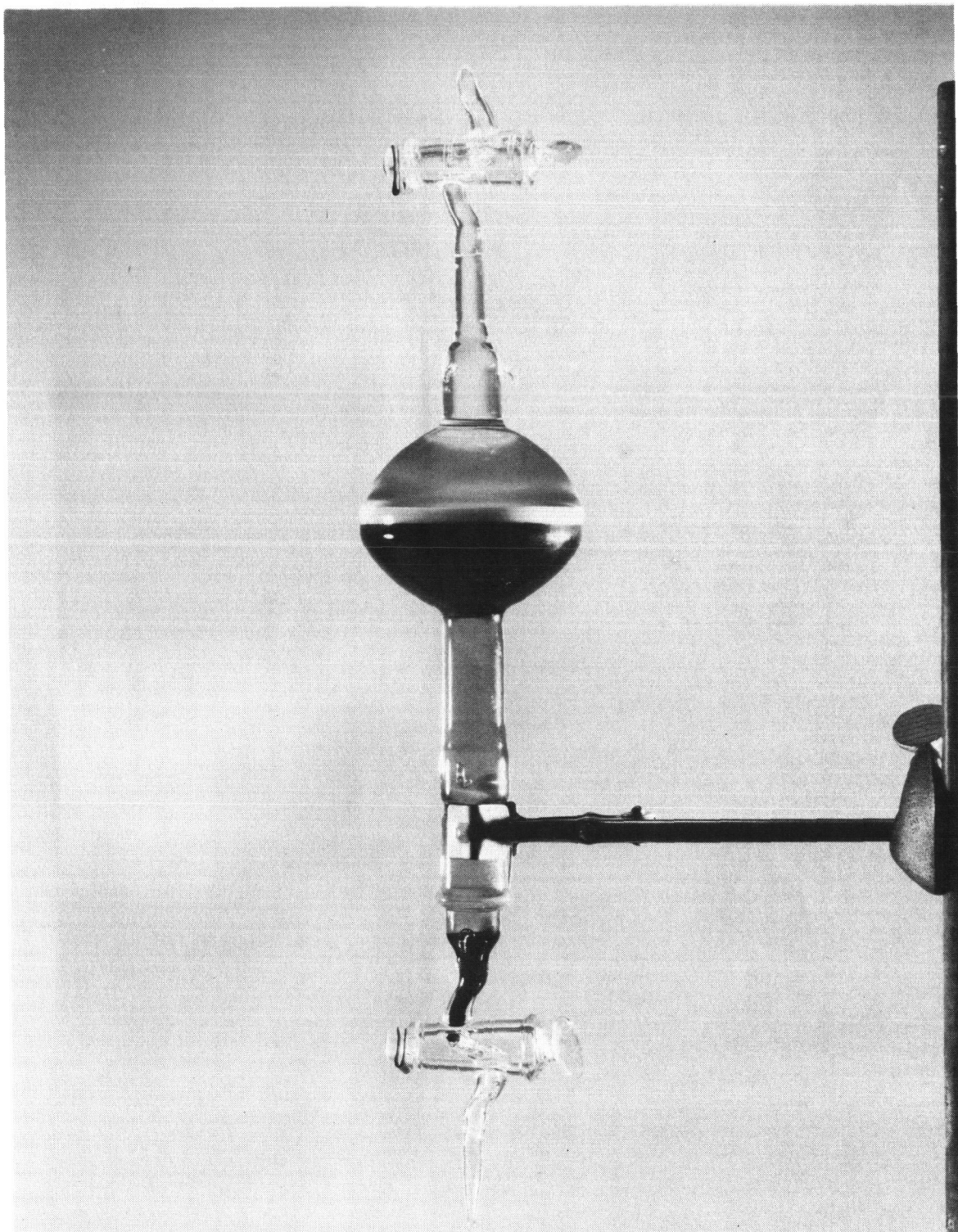
Figure 19. Modified pycnometer for determination of true
density of microspheres.

Effect of Pressure on Flotation

Preliminary attempts to determine the effect of pressure on the flotation of microspheres in water was abandoned because the spheres slowly absorbed moisture and sunk. Therefore the effect of pressure on flotation using toluene was determined on a sample of microspheres, Batch No. C505. A one-gram sample of microspheres dried for two hours at $160^\circ F$, is placed in a large separatory funnel and 400 ml of water containing 2 drops of Cenco wetting agent was added. After stirring thoroughly, the mixture is allowed to stand for 10 minutes. The microspheres which have settled are collected on a dried, weighed filter paper and weighed after drying to constant weight at $225^\circ F$. Additional water is added to the separatory funnel to replace the amount lost during separation of the settled microspheres. (See Figure 20.)

The funnel containing the remaining microspheres is immediately placed in a pressure chamber and nitrogen is admitted until the desired pressure is obtained. The pressure is released immediately.

The microspheres which have settled under pressure are collected on a dried, weighed filter paper and are dried to constant weight at $225^\circ F$. The microspheres which are still floating are similarly collected, dried, and weighed.
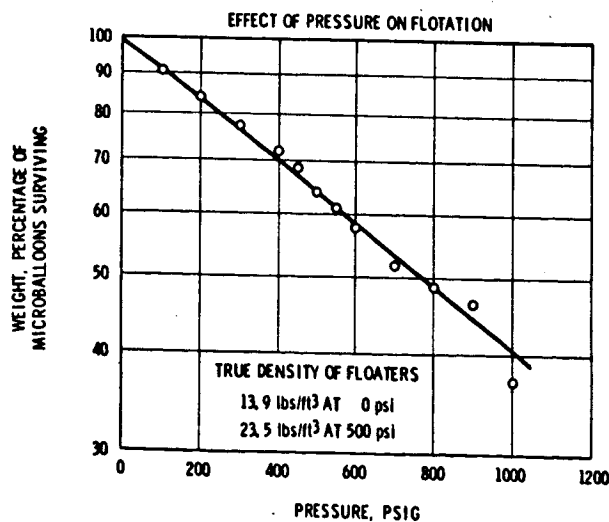
Figure 20. Effect of pressure on flotation of microspheres.

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The pressure was varied from 100 to 1000 psig. In some cases, a fairly large percentage of microspheres were not accounted for. This may be due to mechanical loss of the microspheres during admission of the pressurizing gas. The results are shown in Table 30.

True Density of Pressure-Graded Microspheres

A small quantity of microspheres mixed with toluene was subjected to 500 psig by the use of helium gas. The results of this pressure grading are as follows:

Broken, no pressure	1.80%
Broken, under pressure	35.59%
Unbroken, under pressure	58.49%

The true density of the floaters was determined from pycnometer measurements and found to be 23.21 pounds per cubic foot.

A repeat analysis gave 1.76, 37.87, and 58.68% for the microspheres broken under no pressure, broken under 500 psig and unbroken, respectively. The true density of the floaters was 23.75 pounds per cubic foot.

Analysis of the Effect of Pressure on Microspheres

The strength of Microspheres is of concern when this material is to be used as a molding material filler. It was thought that this property could be approximated by determining the pressure required to collapse the Microspheres.

Data were collected on the effect of hydrostatic pressure (in toluene) upon the buoyant weight fraction of microspheres. The measurements consisted of weighing the fraction of microspheres floating at each value of a non-arithmetic sequence of pressures ranging from 100 psig to 1000 psig. In each case a zero pressure control was weighed. At a given pressure both measurements were made on three separate specimens of material.

In order to determine the nature of the distribution as rapidly as possible graphical screening methods were employed. It was evident immediately that neither a normal nor a log normal distribution applied.

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Pressure, Psig	Percentage* Settled, No Pressure	Percentage* Settled Under Pressure	Percentage* Floating Under Pressure	Percentage* Unaccounted For
100	1.66 (1.70, 1.63, 1.66)	6.33 (6.47, 6.42, 6.1)	90.47 (90.04, 90.49, 90.88)	1.40 (1.39, 1.46, 1.34)
200	1.70 (1.77, 1.64, 1.68)	11.28 (11.33, 11.32, 11.20)	84.20 (84.40, 84.08, 84.10)	2.83 (2.50, 2.99, 3.01)
300	1.57 (1.52, 1.62, 1.56)	17.91 (17.66, 18.42, 17.65)	77.52 (77.72, 77.31, 77.52)	3.18 (3.10, 3.17, 3.27)
400	1.60 (1.68, 1.65, 1.48)	25.05 (25.35, 24.95, 24.84)	72.12 (72.10, 72.15, 72.11)	1.53 (1.79, 1.25, 1.56)
450	1.58 (1.52, 1.58, 1.65)	27.54 (27.89, 27.47, 27.26)	68.50 (67.55, 68.97, 68.98)	2.04 (2.04, 1.98, 2.11)
500	1.67 (1.65, 1.68, 1.68)	33.16 (33.49, 32.53, 33.46)	63.87 (63.71, 64.13, 63.78)	1.30 (1.18, 1.65, 1.08)
550	1.64 (1.68, 1.65, 1.60)	35.75 (36.03, 35.62, 35.59)	61.00 (60.86, 60.92, 61.24)	1.60 (1.42, 1.81, 1.57)
600	1.64 (1.66, 1.62, 1.64)	39.32 (39.25, 39.36, 39.34)	57.63 (57.95, 57.84, 57.10)	1.35 (1.09, 1.17, 1.80)
700	1.56 (1.57, 1.58, 1.53)	45.79 (45.80, 45.75, 45.82)	51.69 (51.73, 51.62, 51.73)	0.94 (0.90, 1.01, 0.92)
800	1.40 (1.27, 1.46, 1.47)	49.08 (49.22, 48.97, 49.05)	48.70 (49.03, 48.23, 48.85)	0.82 (0.47, 1.34, 0.64)
900	1.43 (1.25, 1.83, 1.22)	51.71 (52.21, 52.70, 50.21)	46.18 (45.32, 45.16, 48.07)	0.64 (1.10, 0.31, 0.50)
1000	1.35 (1.26, 1.49, 1.30)	60.69 (60.68, 60.81, 60.56)	37.09 (37.02, 37.12, 37.14)	1.36 (1.04, 1.95, 1.09)

*Figures in parentheses are individual values

Table 30. Effect of pressure on flotation of phenolic
microspheres.

However an exponential distribution apparently provided an excellent
fit to the data. This is shown in Figure 20 where the means of the
weight percent surviving a given pressure have been plotted against
that pressure.

Note that a log relationship is strongly indicated. Thus the
distribution can be approximated by an equation of the form

$$\ln f = K P + C$$

where f is the weight fraction surviving application of a pressure, P, and K and C are constants. If all of the microspheres floated at zero pressure then C would be zero but since such is not the case, this constant must also be estimated.

Since the data had been collected in sets of six readings, it was decided to estimate the parameters by at least squares technique involving pooling of variances and covariances within sets. This procedure would tend to "average out" the effects of possible trends upon the estimate of the slope.

The calculations yielded the following estimates:

R (correlation coefficient) = -0.997

$K = 8.89 \times 10^{-4} \, in^2/lb$

$C = -1.50 \times 10^{-2}$

(The correlation coefficient is highly significant at a level of P less than .001).

The relationship can be expressed as

$$f = 0.985 \, C^{-8.89 \times 10^{-4} \, P}$$

That is, 0.985 is the mean weight fraction of microspheres floating at zero pressure. (1.5% by weight are probably broken microspheres or "sinkers" in the as-received condition.)

By analogy with "half-life" in the disintegration of radioactive materials we can express the slope in terms of "half-pressure" or pressure required to reduce the weight fraction of survivors by 50%. This "half pressure" value is 770 psi. It should be noted that this does not necessarily correspond to a median if the latter is defined as that value of pressure at which the number of survivors are reduced by 50%.

Since the material is molded under a force which would be equivalent to a hydrostatic pressure of 2000 psi within a material behaving as a fluid it was thought that it would be of interest to extrapolate the above equation to this condition. The weight percent of survivors was 16.6.

The true density of the microspheres was determined for the floaters at 0 psi and 500 psi. As expected the density of the 500 psi survivors was considerably higher than the unpressurized material.

True Density of Floaters at 0 psi   13.9 lbs/ft^3

True Density of Floaters at 500 psi   23.5 lbs/ft^3

Effect of Pressure Grading on Sieve Fractions of Microspheres

Two sieve fractions were subjected to helium at a pressure of 500 psig:

- passed 30 mesh, retained on 50 mesh
- passed 170 mesh, retained on 230 mesh

The results of this pressure grading, for the two sieve fractions are shown in Table 31.

As expected, a much larger percentage of the finer mesh microspheres withstood pressurization without breaking.

The true density was determined of the original sieve fractions and of the floaters from both sieve fractions. The results obtained are shown in Table 31.

Flotation Analysis of Microspheres Tested at 100 and 300 psi

In order to check the possibility of up-grading microspheres by pressurization at low pressures, a determination was made of the fraction broken and density of floaters after subjection to 100 and 300 psi. The data is summarized below.

	True Density of Floaters Lbs/cu ft	Percent °F Floaters
As Rec'd (16.1 lbs/ft^3)		1.8
After 100 psi	15.5	90.4
After 300 psi	21.9	79.1

Sieve Fraction	Percentage Settled, No Pressure	Percentage Settled, Under Pressure	Percentage Floating, Under Pressure	True Density, Lbs/Cu Ft	
				Original Fraction	Floaters
80	1.74	53.74	44.22	13.9	27.0
230	2.90	30.49	66.99	15.7	28.6

Table 31. Effect of pressure on sieve fraction of microspheres.

Effect of Sieving and Drying on Density of Microspheres

Two experiments were run to determine (1) if the drying of Microspheres caused serious damage and (2) if eliminating the very large (+50 mesh) and very small microspheres would seriously affect density. The data is summarized below:

	As Received	After Drying 3 hrs @ 225°F	-50 Mesh and +230 Mesh
True density, lbs/ft^3	16.1	16.5	15.9
Fractured microspheres (sinkers) at 0 psi - %	1.79	1.81	.33

From the above data it was concluded that drying the microspheres caused little damage and that sieving was a satisfactory method of up-grading. Evidently the use of the 50 mesh screen eliminates the large spheres and agglomerates; and the 230 mesh screen separates most of the broken fragments and very small high density spheres.

The yield which would be obtained sieving the Microspheres (-50 mesh and +230 mesh) was determined as follows:

Wt-% Microspheres retained on 50 mesh   0.33

Wt-% Microspheres passed 50 mesh retained on 230 mesh   90.05

Wt-% Microspheres passed 230 mesh   9.15

Thermogravimetric Analysis

TGA was performed at Hughes on samples of phenolic microspheres from two different batches. The degradation curves for the

two samples were identical. A typical TGA curve is shown in Figure 21. The curve is typical of phenolic materials.

Summary of Characteristics of Phenolic Microspheres

The phenolic microspheres were found to have a wide particle size variation following a normal distribution except for a small fraction of large agglomerates and fractured particles. The true density of the spheres was found to vary from 13.5 to 16.5 lbs/ft^3. The ash content was high and contained a large proportion of sodium. The spheres were found to be easily damaged by hydrostatic pressure and the large diameter spheres were more susceptible to damage than the small. The data on microspheres is summarized in Table 32.

Property	Value
Volatiles (as received)	5%
Ash Content	5%
Major Constituent of Ash	Sodium
True Density	13.6 to 16.5 lbs/ft^3
Bulk Density	5.24 lbs/ft^3
Susceptibility to Hydrostatic Pressure	
% Floating at 100 psi	90%
500 psi	61%
1000 psi	37%
Particle Size Distribution	
2% Smaller than	0.0017 inch dia
0.5% Larger than	0.016 inch dia
Balance evenly distributed	

Table 32. Summary of characteristics of phenolic microspheres.
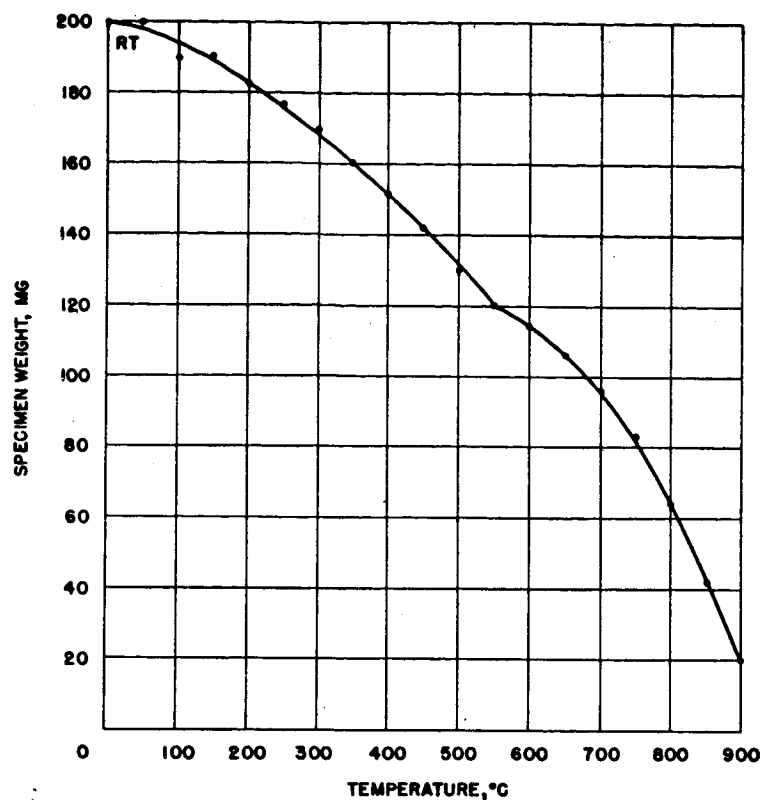
Figure 21. Thermo gravimetric analysis of
phenolic microspheres.

2.4.3 Powdered Nylon 66

The purity and uniformity of the powdered Nylon 66 was expected
to be high because this polymer is produced continuously on a large
scale to exacting specifications. This prediction proved to be true as
shown by the following data.

Apparent or Bulk Density

The bulk density was measured with the same procedure
described for the resin and phenolic microspheres. (See Table 33.)

Melting Point

The melting point was determined on six samples taken from
various locations in a drum of 80 mesh Nylon 66. Two determinations

Treatment	Net Wt-Gm	Density Gm/cc
Vibration Compacted	62.3	.561
Vibration Compacted	55.5	.500
Vibration Compacted	59.4	.535
Average		.532
No Compaction	55.9	.504
No Compaction	52.7	.472
No Compaction	52.4	.472
Average		.484
No Compaction	55.8	.503
High Humidity	57.0	.514
High Humidity	54.2	.488
Average		.502

Table 33. Bulk density of powdered Nylon 66 - 80 mesh.

were made on each sample using a Fisher-Johns melting point apparatus. Table 34 gives the melting point values obtained.

Sample Designation	Location of Sample in Drum	Run No.	Melting Point, ^{o}C
XNBO	Bottom, outside	1	258
		2	257
XNBC	Bottom, center	1	258
		2	257
XNCO	Center, outside	1	257
		2	257
XNCC	Center, center	1	255
		2	254
XNTO	Top, outside	1	254
		2	255
XNTC	Top, center	1	255
		2	256

$$\bar{x} = 256.1$$
$$s = \pm 1.4$$

Table 34. Melting point of Nylon 66 - 80 mesh.

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Volatiles

Volatiles determinations were made on six samples taken from various locations in a drum of 80 mesh Nylon 66. Two determinations were made on each sample. Initially, the weight loss was determined after 30 minutes at 300°F. An additional 15 minutes at 300°F resulted in no additional weight loss. Table 35 summarizes the results.

Ash Content and Spectographic Analysis of Ash

The ash content of the dried samples remaining after the volatiles determinations described in the previous section was determined by ignition to constant weight at 1300°F. The values of ash content in Table 36 are based on the dried weight, not the original weight prior to the analysis for volatiles.

The ash remaining (0.36%) after the ignition of 80 mesh Nylon 66 was subjected to emission spectrographic analysis. Table 37 gives the semiquantitative results based on the ash weight and on the weight before ignition.

Sample Designation	Location of Sample in Drum	Run No.	Volatiles (45 min. at 300°F) Percent
XNBO	Bottom, outside	1 2	0.13 0.14
XNBC	Bottom, center	1 2	0.24 0.33
XNCO	Center, outside	1 2	0.35 0.36
XNCC	Center, center	1 2	0.19 0.22
XNTO	Top, outside	1 2	0.22 0.24
XNTC	Top, center	1 2	0.12 0.12

$$\bar{x} = .212$$
$$s = .105$$

Table 35. Volatile content of Nylon 66 - 80 mesh.

Sample Designation	Location of Sample in Drum	Run No.	Ash Content, Percent
XNBO	Bottom, outside	1 2	0.30 0.33
XNBC	Bottom, center	1 2	0.27 0.28
XNCO	Center, outside	1 2	0.32 0.29
XNCC	Center, center	1 2	0.36 0.31
XNTO	Top, outside	1 2	0.30 0.32
XNTC	Top, center	1 2	0.27 0.38

$$\bar{x} = .311$$
$$s = \pm.034$$

Table 36. Ash content of Nylon 66 - 80 mesh.

Element	Percent (Based on Ash)	Percent (Based on Unignited Weight)
Potassium	37.	0.28
Sodium	4.0	0.030
Copper	0.11	0.0008
Magnesium	0.0017	0.000013
Iron	0.0081	0.000062
Silver	0.0012	0.000009
Chromium	0.0037	0.000028
Calcium	0.035	0.00027
Lithium	0.0057	0.000043
Silicon	0.036	0.00027

Table 37. Spectrographic analysis of ash from Nylon 66.

Total Nitrogen

The total nitrogen was determined on two samples of 80 mesh Nylon 66. Sample XNBC was taken from the bottom-center of the drum and XNTC was taken from the top-center. Two determinations were made on each sample. The values, obtained by the Dumas method, are shown in Table 38.

Nylon Sieve Analysis

Particle size and distribution measurements were made for nine samples of nylon 66. One sample was run from each of six locations in the drum received from Liquid Nitrogen Processing, Malvern, Pennsylvania. The specific locations were at the top, center and bottom of the drum with one set along an outside edge and one set along the center axis. Originally, one sampling was made at each location, however, when the data appeared to be non-uniform an additional set of three samples were made to verify the non-uniformity within the drum.

The sieving was accomplished with a Tyler Rot-A-Tap and six sieves. The sieve numbers and their corresponding maximum hole sizes are as follows: 50 - 0.0116", 80 - 0.0070", 120 - 0.0049", 170 - 0.0035", 230 - 0.0024", and 325 - 0.0017". The lower pan caught all particles smaller than 0.0017". The results of the sieving are shown in Table 39.

The cumulative weight percentages of material coarser than a given mesh opening were calculated for the nine specimens and plotted on probability graph paper (see Figures 22 and 23). It should be pointed

Sample Designation	Run No.	Total Nitrogen, Percent
XNBC	1	11.72
	2	11.51
XNTC	1	11.92
	2	11.87

Table 38. Total nitrogen content of Nylon 66.

Percentages on Each Sieve

Sieve No.	Top Center		Center Center	Bottom Center	
50	21.39	23.03	12.26	3.32	2.29
80	40.96	39.83	35.03	19.25	14.23
120	14.68	15.39	22.02	23.11	21.33
170	7.08	6.81	10.73	18.20	19.51
230	4.58	4.26	6.49	10.64	13.16
325	4.29	4.28	5.78	9.99	12.45
Pan	7.01	6.40	7.69	15.49	17.04
	Top Outside		Center Outside	Bottom Outside	
50	21.55		14.76	6.79	7.00
80	36.84		41.49	35.55	31.02
120	16.42		18.07	20.48	21.95
170	7.99		8.22	12.62	12.98
230	5.17		4.90	8.53	8.22
325	4.55		4.83	7.13	7.41
Pan	7.49		7.74	8.89	11.43

Table 39. Results of sieving of Nylon 66 - 80 mesh.

out that all plotted data are not of equal statistical weight. The means of two screenings were used in the case of specimens taken at drum wall-bottom, at axis/top, and at axis/bottom. The other plots are based on individual readings.

Note that both figures show some stratification of particle sizes, ranging from coarser at the top to finer at the bottom. Or, more precisely, distributions are centered at higher values at the top than at the bottom but with extremely large overlaps of all distributions.

The figures indicate that it is quite probable that the distribution of particles from a given specimen is normal. It was decided to establish whether such was the case for each of the sieve specimens because this information would be of value later in setting quality control limits.

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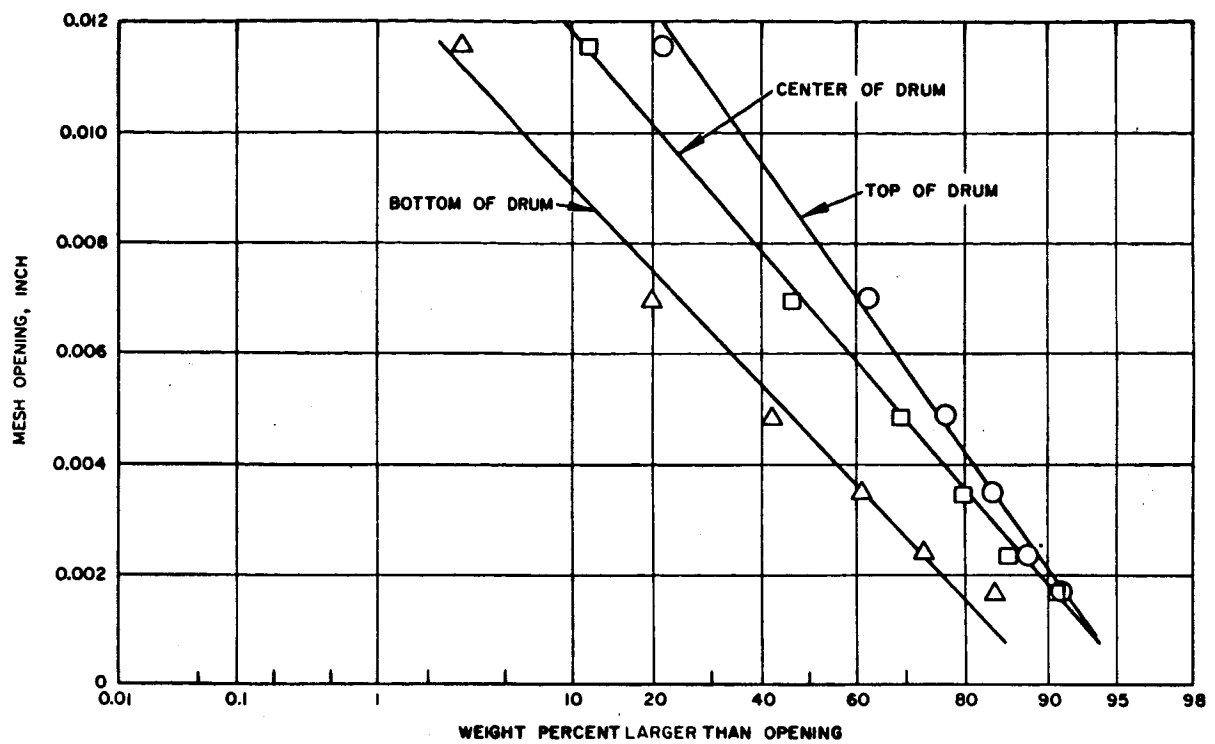
Figure 22. Distribution of particle sizes of Nylon 66 - 80 mesh. Samples taken along drum axis.
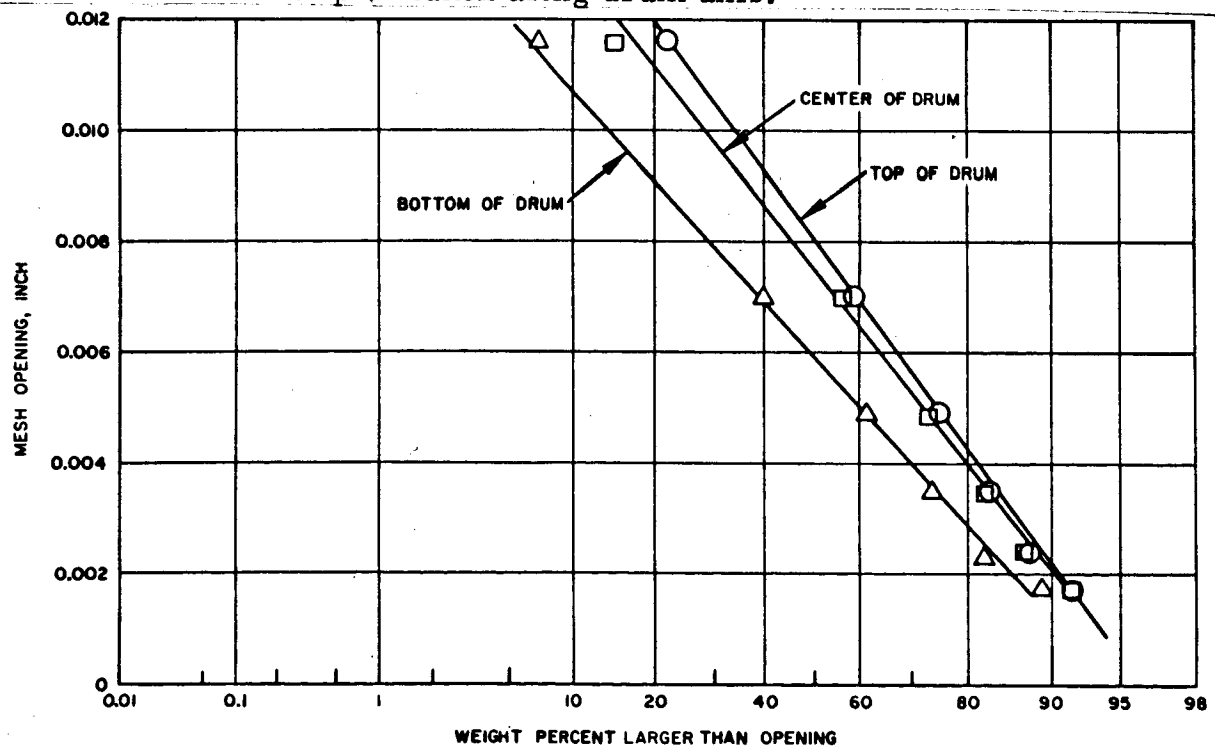
Figure 23. Distribution of particle sizes of Nylon 66 - 80 mesh. Samples taken along drum wall.

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The cumulative weight fraction coarser than each mesh opening was taken as a value of the normal probability integral. From this, the corresponding upper limit of integration, expressed as the deviate of unit variance, was found from tabulated values of the normal probability integral.

If the data of each specimen were normally distributed, then its mesh openings and normal deviates should be linearly related. Therefore if a highly significant coefficient of correlation were obtained then the hypothesis of normal distribution could be accepted.

All nine distributions gave correlation coefficients which were highly significant (P less than .001).

Since the distributions were normal it should be possible to calculate the statistics (mean and standard deviation) of each one. That is, if the normal deviates are expressed as linear (least squares) functions of mesh openings, the constants are related to the statistics. The slope is equal to the reciprocal of the standard deviation and the intercept is the negative reciprocal of the coefficient of variation, from which the mean can be calculated. By these procedures, the values listed in Table 40 were obtained.

Location	Correlation	-inch	Deviation-inch
Top-Axis	+0.9982	.0081	.0045
Top Axis	+0.9985	.0083	.0045
Middle-Axis	+0.9982	.0069	.0039
Bottom-Axis	+0.9952	.0049	.0035
Bottom-Axis	+0.9906	.0043	.0034
Top-Wall	+0.9988	.0080	.0046
Middle-Wall	+0.9785	.0063	.0028
Bottom-Wall	+0.9981	.0062	.0036
Bottom-Wall	+0.9987	.0059	.0038

Table 40. Specimen coefficient of mean standard.

The particle size data has been generalized and shown in Figure 24. It should be noted that these are approximately 10% of particle larger than 50 mesh. This information corresponds to the visual and microscopic observation of large nylon particles in the molded ablators. A typical example is shown in Figure 25.

Thermogravimetric Analysis

The thermogravimetric analysis of Nylon 66 - 80 mesh performed at Hughes gave the expected results for nylon. Rapid weight loss commenced at approximately $300^\circ C$ with only 10 - 15% of material remaining at $500^\circ C$. At $900^\circ C$ only the ash remained. The TGA curves are shown in Figure 26.

Summary of Properties of Nylon 66 - 80 Mesh

The Nylon 66 was found to be uniform in physical properties. The ash content of 0.4% (primarily potassium) is considered a normal residue from the nylon manufacturing process. The particle size distribution for nominally 80 mesh material is wide and contains approximately 10% of particles larger than 50 mesh. It is possible that such large particles may spall or melt during ablation and cause uneven and excessive erosion of the ablating surface. The properties of the nylon are summarized in Table 41.
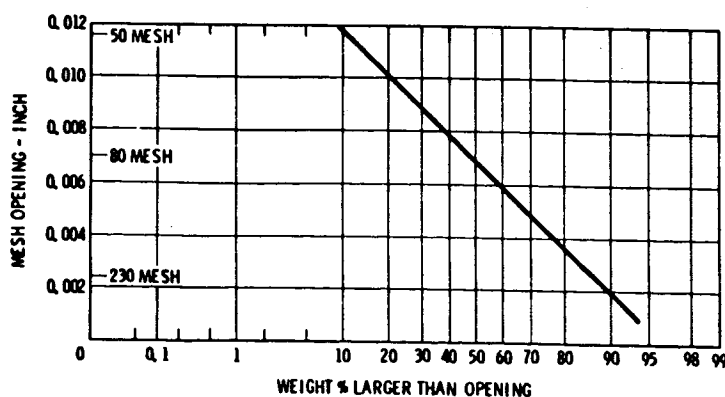
Figure 24. Generalized particle size distribution of Nylon 66 - 80 mesh average.
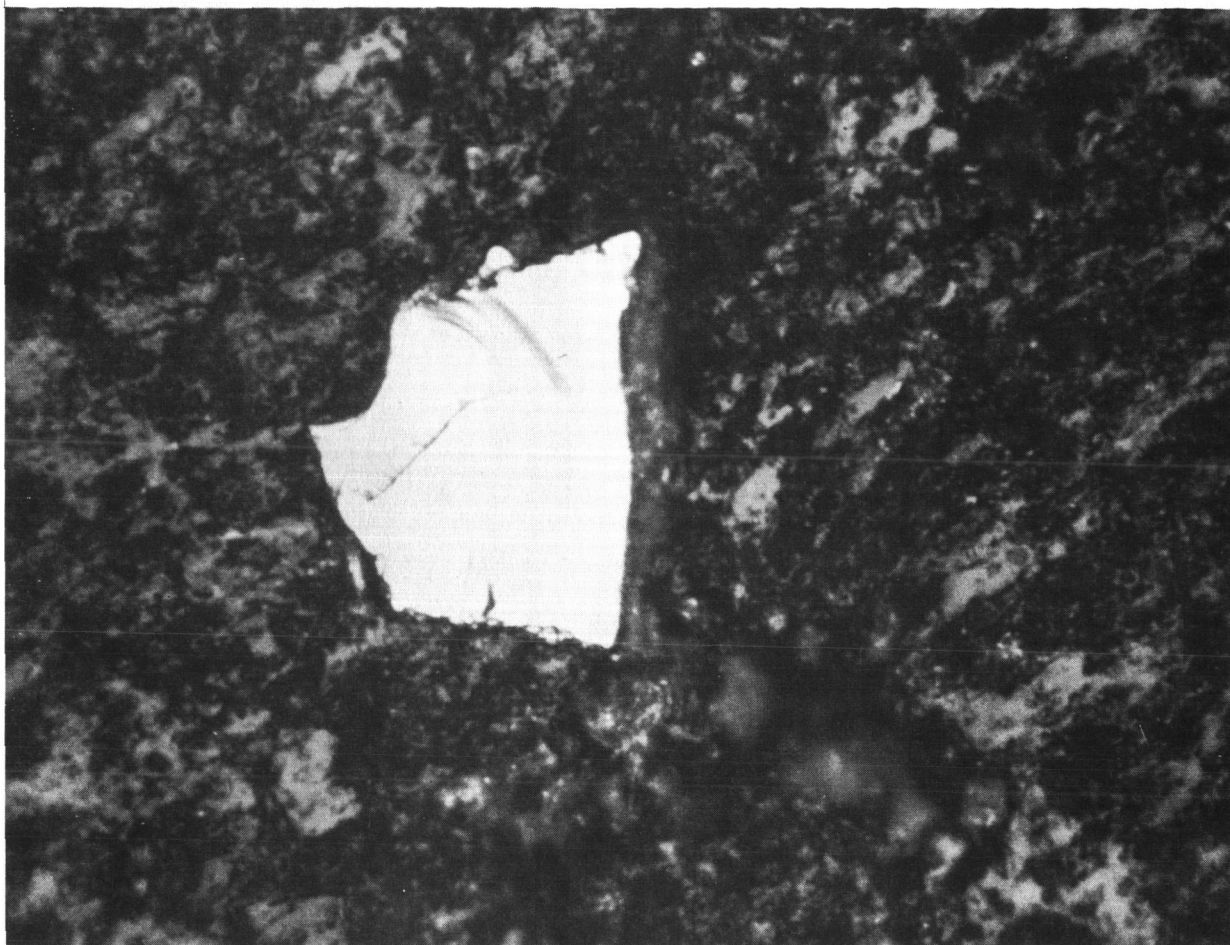
Figure 25. Large nylon particle in fractured surface of
Langley billet - photomicrograph at 400X.

2.4.4 Quality Control Checks on Langley Raw Materials

As directed by the sampling plan, a sample of each raw material
and each batch of formulation was taken by Langley NASA for each
production billet made. These samples were checked by Hughes for
uniformity by simple testing procedures. As expected from the high
degree of control exerted by Langley, the quality control tests showed
good uniformity. The mean, $\bar{x}$, and the standard deviation, s_x, was
calculated for each set of data.
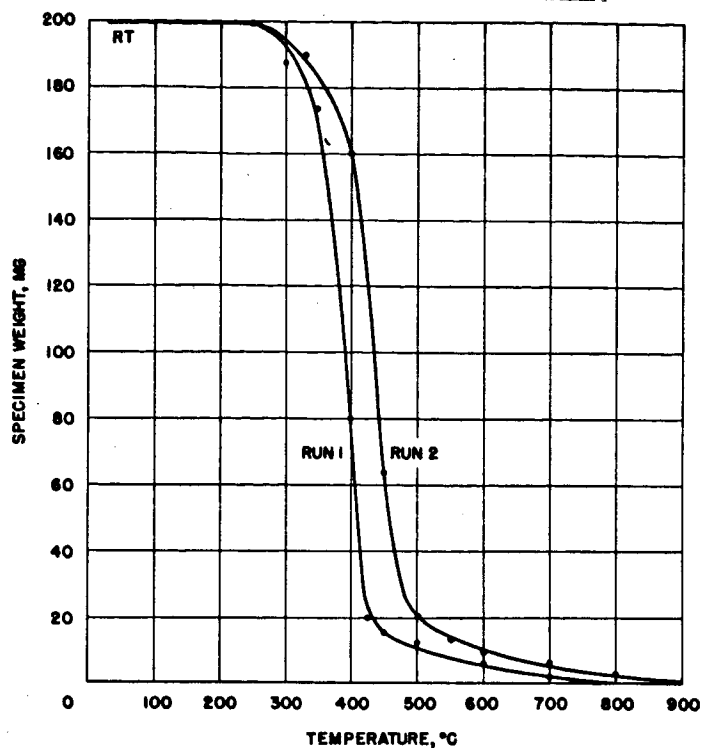
Figure 26. TGA curves of Nylon 66 - 80 mesh at 360°C/hr.

Property	Value
Bulk Density	30.2 lbs/ft^3
Volatile Content (as received)	0.12 - 0.35%
Ash Content	0.36%
Melting Point	256°C
Particle Size Distribution	~ 90% passes 50 mesh ~ 50% passes 80 mesh ~ 87% passes 230 mesh
Total Nitrogen	11.8%

Table 41. Summary of properties of powdered
Nylon 66 - 80 mesh average.

Microspheres

Volatile content and true density tests were performed with these samples. Triplicate samples were removed from each batch of microspheres submitted. Each sample was weighed both before and after drying in an oven at 300°F for 30 minutes. The percent of volatiles was calculated from the formula:

$$\frac{w_i - w_f}{w_i} \times 100$$

where

w_i = initial weight

w_f = final weight

A total of 111 samples were tested. The mean value of the percent of volatiles was 6.549 and the standard deviation was 1.015.

The true density was performed on 14 samples and discontinued. The values were each very consistent with the previous results and the test is tedious and time consuming. The mean value of the true density was 15.07 pounds per cubic foot and the standard deviation was 0.89 pounds per cubic foot.

Phenolic Resin

Volatile content tests were performed on 111 samples of Phenolic resin obtained from 37 batches submitted. The procedure was similar as described above except that the samples were heated from 60 minutes. The mean value of the percent of volatiles was 3.429 and the standard deviation was 0.454.

Molding Formulation

Ash content determinations and model billet moldings were made from the molding formulation batches. Triplicate samples of approximately 10 grams were ignited at 500°F and heated at 1300°F until they reached a constant weight. The mean value of 111 samples was 1.358% Ash and the standard deviation was 0.211.

Billets were molded in a 4 inch diameter by 1 inch high mold. The charge weight was 120 grams. The mean value of density of 37 molded billets was 36.08 pounds per cubic foot and the standard deviation was 0.803 pounds per cubic foot.

2.4.5 Summary and Conclusions of Langley Billet Investigation

The results of the investigation of the Langley Ablator may be summarized as follows:

Raw Materials

- The commercial phenolic novolac is a typical two-step phenolic molding powder with a low degree of inorganic impurities. The amount of unreacted phenol and low molecular weight material in the resin is somewhat high but this may be advantageous in increasing flow during processing. The variability of the resin from batch to batch was not established and remains in doubt.

- The phenolic microspheres contain a high degree of inorganic impurities, primarily sodium ions. The material as received contains a small proportion of fractured microspheres and large agglomerates. The particle size distribution of the microspheres follows essentially a normal distribution and the larger diameter spheres are most susceptible to breakage under pressure. The true density of the bulk material varies from 13.5 to 16.5 lbs/ft^3 from batch to batch and within batches.

- The nylon 66 material is uniform in physical properties. The 80 mesh powder has a wide particle size distribution and contains approximately 10% of particles greater than 50 mesh.

Process

The Langley ablator molding process is well controlled and reproducible. The care taken by Langley is shown by the uniformity of

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the bulk physical properties of the ablator and the small variations in raw material and formulation samples.

Molded Ablator

- The Langley ablators are uniform in density. Real density variation occurred but they are of small magnitude and take the form of a dense outer shell and a lower density core. The billets average approximately 1.5 lbs/ft^3 lower than the 35 lbs/ft^3 density required.

- The Langley Ablator material is low in compressive strength and tensile strength. It is highly porous. The high degree of interconnected voids has been confirmed by gas transmission test, epoxide impregnation, and mercury intrustion methods.

- The microstructure of the Langley ablator is heterogeneous. Large nylon particles, voids, and gaps are present and almost all of the microspheres are fractured. The nylon and microspheres appear to be poorly wetted with resin.

- The uniformity of the production ablators is associated with the fact that only a single batch of each raw material was used. The Langley process is very sensitive to changes in volume fraction of the raw materials, and variations in resin cure speed. Therefore it can be predicted that the present process would produce ablators of widely different properties if other batches of microspheres and resin were used. Conversely, if equivalent ablators are to be produced from new batches of raw materials, the process would have to be modified. Modification of the process would entail a development program for each new batch of raw materials.

It was not the function of this investigation to assess the effect of the Langley ablator's properties on ablation performance. However, it was the intent of this investigation to critically analyze the molded ablator as a plastics composition. From this point of view the formulation and processing of the Scout ablator billets are not optimum. The

formulation is low in volume fraction of resin and high in volume fraction of microspheres. This condition combined with a processing method which causes mechanical damage to the microspheres and large temperature differentials during processing results in a less than optimum plastic material. The high porosity and low mechanical strength may be directly correlated with the formulation and processing of the ablator. The sensitivity of the process to changes in the properties of the raw materials and the known and suspected variation of the raw materials is a cause for concern. A more optimum formulation, based on more uniform raw materials, and a less sensitive process would provide much greater confidence in producing uniform ablators for the future. The phase of the investigation involved in the improvement of the ablator as a plastics composition is described in Section III of this report.

3.0 DEVELOPMENT OF AN IMPROVED NYLON PHENOLIC SYNTACTIC FOAM

The molded ablator material for the Scout Nosecap exhibited several deficiencies as a plastics material. These deficiences may be summarized as (1) low mechanical properties, (2) high porosity, (3) a difficult process, (4) a heterogeneous microstructure, and (5) variability of raw materials. The part of the program concerned with improving the ablator was carried out during and after the characterization of the Scout material. Therefore many of the changes described here instituted orginally on the basis of experience or insight into the problem before confirming data was developed from the characterization of the Scout ablator. The improvements were based on the following approaches.

- Upgrading of the raw materials to reduce variability and to increase the uniformity of the microstructure of the molded material.

- Modification of the formulation to produce a mixture less subject to damage during processing, more amenable to processing, and to provide improved mechanical properties in the final product.

- A complete change in the molding process to provide more rapid and uniform curing, less degradation of the raw materials, and molding-to-size of the Nosecap.

All of these changes are interrelated. It is not possible to separate raw materials, formulation and processing and clearly delineate the effect each change has in the final product. However, the interaction of the various changes will be described as much as possible in the following section.

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3.1 UPGRADING OF RAW MATERIALS

3.1.1 Phenolic Novolac

A decision was made early in the program to develop a reproducible analog of the single batch of commercial novolac used in the production of molded billets. This decision was not based on any criticism of the commercial novolac which, as proved during characterization, is a pure and high quality product. The decision was based primarily on the uncertainty of securing future batches with the same properties. Therefore, a synthesis effort was carried out to duplicate the commercial novolac within narrow limits. This was followed by the production of several hundred pounds of the resin at a local commercial resin plant under closely controlled conditions.

Synthesis Effort

The properties of phenolic novolacs are controlled primarily by the ratio of the weight of phenol to the weight of 37% formaldehyde solution in the initial reaction mixture. All of commercial novolacs are made in the range of 6.8 to 7.2 phenol/formaldehyde ratio. The experimental approach to duplicating the commercial novolac was therefore to produce two standard resins which would bracket the average molecular weight range of the commercial resin. The properties of these resins were to be compared with the commercial material and it would then be possible to zero-in on the commercial material. Provided pure reactants and normal reaction conditions were used, a knowledge of the average molecular weight, and free phenol content should be sufficient to empirically duplicate the commercial novolac.

The two standard novolacs were therefore synthesized using raw materials of the same quality as used commercially. These materials were designated LFN for the low (6.8) phenol/formaldehyde ratio and

HFN for the high (7.2) phenol/formaldehyde ratio. The reaction mixtures were as follows:

	Low Factor Novolac (LFN) F/P = 6.8	High Factor Novolac (HFN) F/P = 7.2
Phenol	4000 g.	4000 g.
Formalin (37%)	2720 g.	2880 g.
Oxalic Acid	40 g.	40 g.

42040 g. < Yield < 4400 g.   4320 g. < Yield < 4440 g.

The various laboratory preparations are described in Appendix VI.

Characterization of Laboratory Novolacs

Infrared Spectra

Infrared spectra of the LFN and HFN resins were compared with that of the commercial novolac both with and without hexamethylene-tetramine. (Figure 27). The spectra of the two Hughes novolacs were found to be essentially identical both as to wavelength of the observed absorption bands and as to their relative intensities. Differences had been expected in the 9.5 - 10.0 micron region of methylol group absorption and at 14.4 microns where absorption indicative of free phenol occurs. Such differences were not found in the spectra of the LFN-1 and HFN-1 novolacs. Also comparison of these spectra with those of the commercial novolac (with and without hexa) indicated that the commercial novolac had been approximated in composition and resin advancement.

These results indicated that infrared spectral analysis was not a satisfactory characterization method for differentiation of structural and chemical characteristics of unfractionated phenol-formaldehyde novolacs. For this reason, it was planned to employ a simple frac-tionation technique with the novolacs and following this, to characterize the several fractions as to number average molecular weight, Mn,

COMMERCIAL PHENOLIC NOVOLAC WATER EXTRACTED

HFN-I PHENOLIC NOVOLAC

COMMERCIAL PHENOLIC NOVOLAC WITH HEXA AND LFN-I WITH HEXA
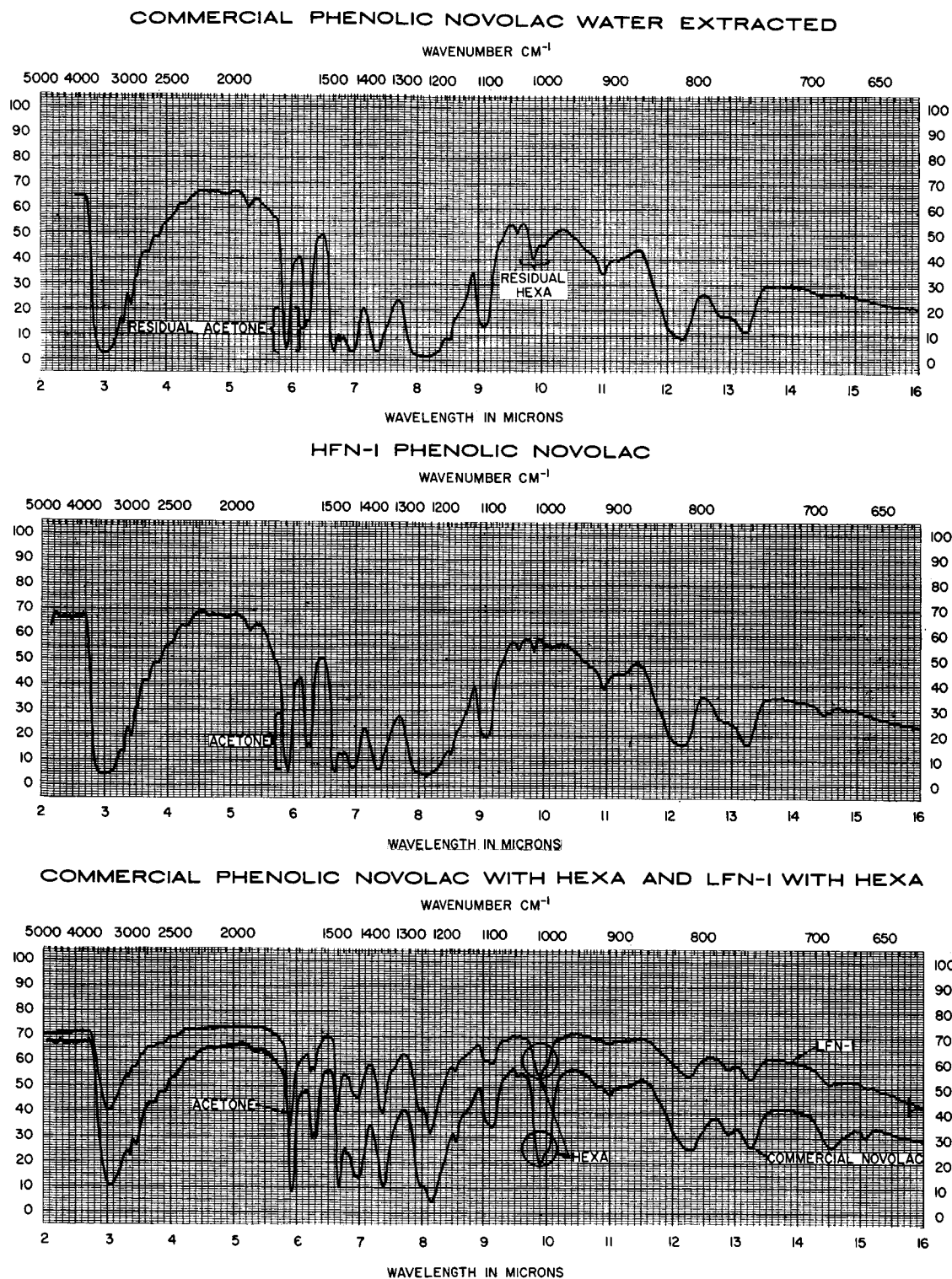
Figure 27. Typical infrared spectra of phenolic novolacs.

and absorption spectra. It was anticipated that this procedure would prove an effective means of characterizing differences between high and low factor novolacs.

Three molecular weight fractions were prepared from the washed commercial novolac by progressive precipitation from acetone solution by addition of water. The IR spectra of the three fractions are shown in Figure 28. The spectra of fractions of the Hughes novolacs were not prepared however because of time limitation and other procedures proved to be more quantitative.

Molecular Weight Determination

The Rast method of molecular weight determination, based on the depression of the freezing (melting) point of camphor, was studied as a possible technique for determining the molecular weight of phenolic novolacs. Although early tests were encouraging, in yielding reasonable and reproducible values for the molecular weight of low factor novolac-3 (680 and 618, in two consecutive runs), subsequent tests with m-terphenyl, gave incongruous results. Because there was insufficient time to perfect the techniques to the required level of accuracy, this method was abandoned in favor of the boiling point elevation method.

Preliminary ebullioscopic measurements were made employing acetone as a solvent. Molecular weights in the range of 770 were obtained for the high factor novolac, however this data was not obtained at ideal conditions. The low K_b value the relatively low boiling point, and the high volatility of the acetone caused many problems. Molecular weight determinations were continued using dioxane as the solvent since it had less volatility, a higher K_b and a higher boiling point. The final procedure is described in Appendix III, Item 3.

The results of the molecular weight determinations are summarized in Table 42.

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HIGH MOLECULAR WEIGHT FRACTION OF COMMERCIAL PHENOLIC NOVOLAC

WAVENUMBER CM⁻¹

INTERMEDIATE MOLECULAR WEIGHT FRACTION OF COMMERCIAL NOVOLAC

WAVENUMBER CM⁻¹

LOW MOLECULAR WEIGHT FRACTION OF COMMERCIAL PHENOLIC NOVOLAC

WAVENUMBER CM⁻¹
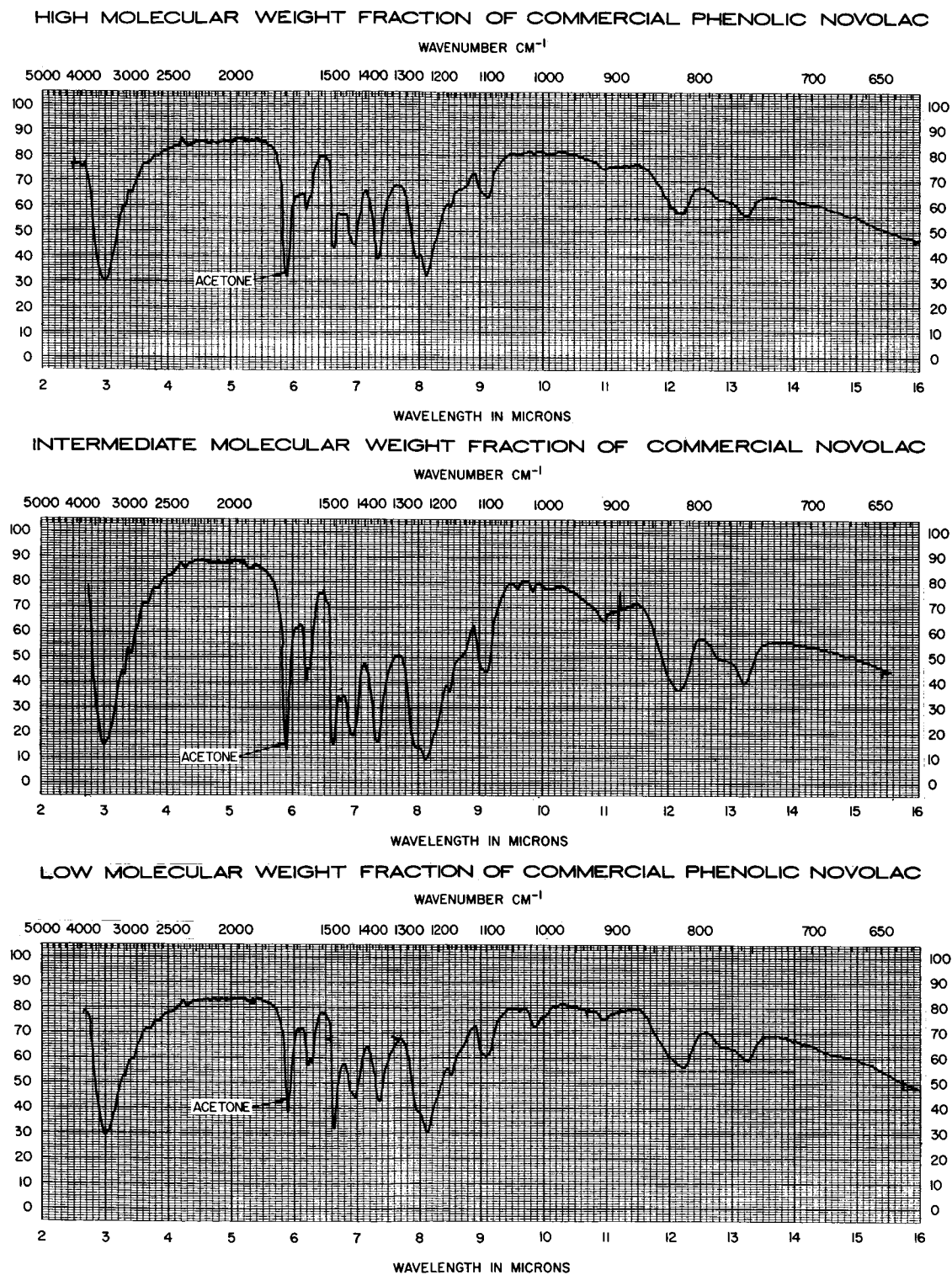
Figure 28. Infrared spectra of molecular weight fractions
of commercial phenolic novolac.

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	Number Average Molecular Wt. at 0 Concentration
HFN	794.4
LFN	606.2
Commercial novolac washed and dried	1337.4
Commercial novolac corrected for loss of low molecular Wt fractions and phenol	800 approx.

Table 42. Summary of molecular weight determinations.

Melting Point

The melting point of Hughes novolacs and water extracted commercial novolac were determined. Results shown in Table 43.

Gel Time

The gel time for LFN-3 and HFN-2 Novolacs was determined at 302°F after adding 9% by weight of hexamethylene tetramine. The results are shown in Table 44.

Viscosity Measurements

Viscosity and Viscosity Index measurements of the Hughes novolacs confirmed that the HFN series of resins was virtually identical to the commercial novolac. Solution viscosity measurements at several concentrations in isopropyl alcohol produced almost identical results for HFN and the commercial material. A plot of concentration against the natural logarithm of the relative viscosity divided by the concentration according to the Houwink and Claasens Relationship (Ref. 9) revealed a striking similarity between the HFN and the commercial novolacs (see Figure 29).

HFN-2

Vacuum Dried 3 hours and Tumbled Before Testing:

Test No.	1	2	3
First Melting Point	89°C	89°C	89°C
Gel Point	87°C	87°C	87°C
Second Melting Point	93°C	93°C	93°C

LFN-3

Same Conditioning as Above:

First Melting Point	79°C	79°C	79°C
Gel Point	77°C	77°C	77°C
Second Melting Point	84°C	84°C	84°C

Commercial novolac water extracted

Same conditioning as above:

First Melting Point	114°C	114°C	114°C
Gel Point	112°C	112°C	112°C
Second Melting Point	120°C	120°C	119°C

Table 43. Melting points for HFN-2, LFN-3 and water extracted commercial novolac.

Production Batch of Hughes LFN

Based on the accumulated evidence it was decided that the HFN resin was a very close approximation of the commercial novolac. A contract was therefore let to a local resin manufacturer, for the production of 800 pounds of Hughes High Formaldehyde Factor (HFN) novolac. Considerable care was taken by this company in cleaning their stainless steel reaction kettle prior to synthesis of the first batch.

Determination	1	2	3
LFN-3			
Time	1 Min.	1 Min.	1 Min.
Minutes & Seconds	35 Sec.	30 Sec.	32 Sec.
HFN-2			
Time	1 Min.	1 Min.	1 Min.
Minutes & Seconds	50 Sec.	48 Sec.	51 Sec.

Table 44. Gel time of HFN and LFN
phenolic novolacs.
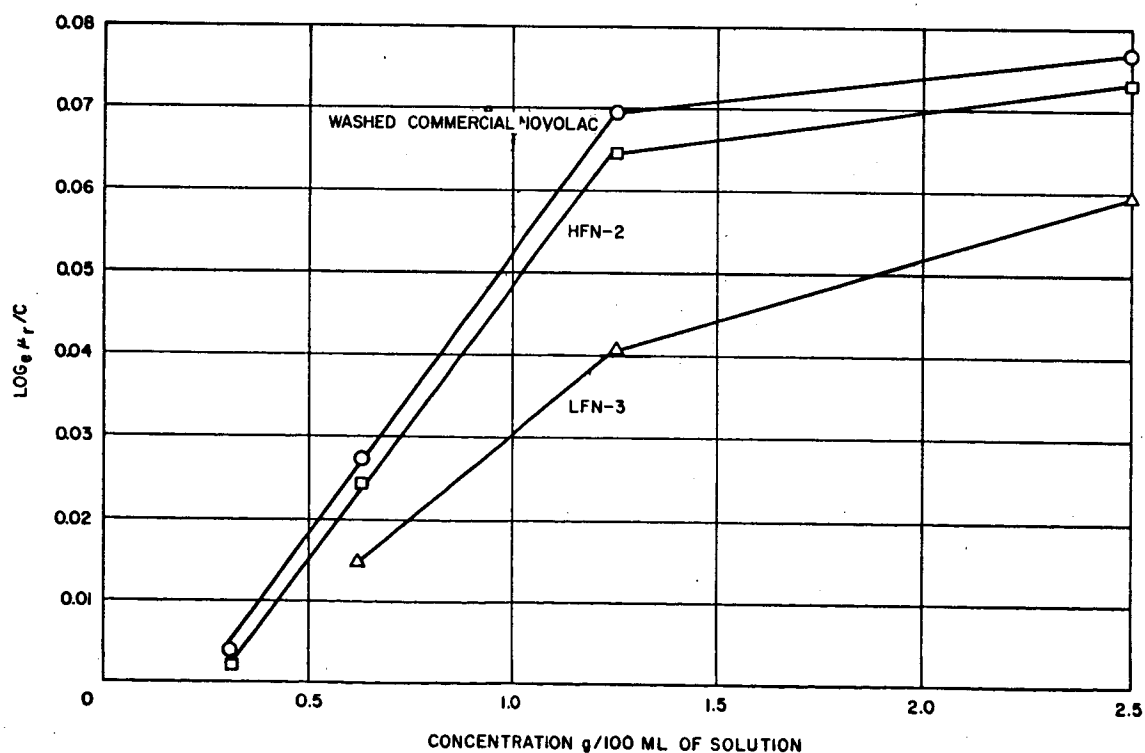
Figure 29. Relative viscosity of novolacs
vs concentration.

The first two batches of 250 pounds each were unsatisfactory. Very short gel times without Hexa and high viscosities were obtained. The material appeared to be a resole rather than a novolac. It was decided therefore that a much higher formaldehyde to phenol ratio was occurring than had been specified. At first it was believed that the assay of the formaldehyde was low due to the presence of formic acid. Analysis at Hughes however showed that the formic acid content was very low. It was then decided to assay both the phenol and the formaldehyde used by Applied Plastics. The phenol proved to be very pure but Applied's assay of the formaldehyde was low by 3 percent.

Subsequent batches of novolac using the revised assay figures were of acceptable quality. A comparison of the properties of the large batch of HFN with the commercial novolac is shown in Table 45.

	HFN Production Batch	HFN With Hexa	Commercial Novolac (extracted)	Commercial Novolac With Hexa
Melt Point Temp. °C	109		114	
Gel Time, Secs. at 300 ± 2°F	78 hrs	131.2	2 hrs	130 Avg.
Viscosity Number		2.1		2.1-2.3

Table 45. Comparison of HFN production batch with commercial novolac.

We were therefore satisfied that the HFN is a close approximation of the commercial novolac.

The procedure for manufacturing the large batches of HFN is detailed in Appendix V. Of the 800 pounds of novolac produced to specification 400 pounds were delivered to NASA Ames in the ungraded condition (without Hexa). Most of the remainder was ground to 250 mesh with Hexa for use at Hughes. Twenty five pounds of the ground resin with Hexa were delivered to NASA Langley.

Ash Content of Hughes Novolac

Analysis of HFN and LFN laboratory batches showed a somewhat higher ash content than the commercial novolac as is shown in Table 46.

Description	Ash Content, Percent
HFN-1	0.070
LFN-1	0.076
Hexemethyl-enetetramine	0.0019

Table 46. Ash content of Hughes novolac.

Ash content of the phenol and formaldehyde used was found to be extremely low. The constituents of the ash as measured semi-quantitatively with a 1.5 meter emission spectograph having a dispersion of 7Å/mm are shown in Table 47. The fairly high ash content in the Hughes synthesized resins is typical of materials made in glass vessels.

Ash contents determined on the HFN production batches also showed inorganic impurities of the order of 0.070%. In this case however the contaminants were high in iron and heavy metals, similar to the impurities found in the commercial novolac. The constituents of the ash were typical of resins made in stainless steel equipment and the higher ash of the LFN compared to the commercial novolac is believed to be due to small size of the batches. In small batches the area of the reaction kettle wall exposed to corrosion is high compared to the volume of mix and therefore more contaminants are absorbed than in large batches.

Specifications

The specification for both the commercial novolac and the HFN resin is contained in Appendix VII.

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Element	Composition Per Cent		
	HFN-1	LFN-1	Hexamethyl-enetetramine
Silicon	0.0098	0.0152	0.0003
Antimony	0.0017	0.00076	0.0002
Calcium	0.00062	0.00099	0.0001
Chromium	0.00020	0.00091	0.000005
Aluminum	0.00054	0.0017	0.0001
Phosphorus	0.0091	0.012	--
Boron	0.000038	0.00023	0.000006
Iron	0.00046	0.00043	0.0002
Magnesium	0.00029	0.00046	0.00005
Manganese	0.00017	0.00065	0.000004
Lead	0.00010	0.00015	0.00001
Nickel	0.00024	0.00020	0.00004
Titanium	0.00010	0.00008	0.00002
Copper	0.000037	0.000046	0.000003
Sodium	0.0020	0.0013	--
Zinc	0.00016	0.00025	0.00001
Zirconium	0.000066	0.000017	0.000001
Cobalt	0.00007	--	0.000002
Strontium	0.000010	0.000017	0.000001
Tin	0.000033	0.0011	0.000005
Molybdenum	--	0.0012	--
Potassium	--	--	--

Table 47. Spectrographic analysis based on unignited weight.

3.1.2 Phenolic Microspheres

The data accumulated in characterizing the microspheres pointed directly to means of upgrading the material. It had been found that the microspheres as received contained small percentages of large agglomerates and fractured spheres. Also, it had been demonstrated that the

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large diameter spheres were most susceptible to damage from hydro-static pressure. Therefore it was possible to obtain a more useful grade of microspheres by flotation and pressurization by discarding the material which sunk. All attempts to locate materials handling equipment which would perform such an operation in bulk were unsuccessful. It was therefore decided to eliminate the large agglomerates, the large diameter microspheres, and the fractured spheres by simple sieve fractionation. Upgraded microspheres were obtained by using only that material which passed through a 50 mesh sieve and was retained on a 230 mesh sieve.

3.1.3 Powdered Nylon 66

Upgrading of the powdered Nylon 66 was accomplished by changing the particle size distribution. Instead of 80 mesh average material, the Nylon 66 was ground to a mesh number particle size under liquid nitrogen by a local vendor. Only that material which passed a 120 mesh sieve was used in the Hughes formulation.

3.2 MODIFICATION OF THE FORMULATION

Two conclusions on the formulation of the molded billet material were drawn from the data collected during the characterization. First, that the volume fraction of resin in the formulation was too low to completely wet and bind together the nylon particles and microspheres; second, that the volume fraction of microspheres was too high and mechanical crushing of them is inevitable in order to achieve the desired density of thirty five pounds per cubic foot.

Recognition of the problems involved in the formulation would normally imply than an empirical approach be taken to produce a more balanced formulation. A series of formulations would be made up with increased resin content and decreased microsphere content. Each of these formulations would be molded with the necessary changes in molding procedure, and thoroughly tested. The formulation which exhibited the best properties would then be selected. An empirical approach of this type would have been inordinately expensive and time consuming.

A mathematical approach was therefore taken to the problem. Ideally the volume fractions in the formulation should add up to unity. For a unit volume of material

$$\frac{\text{Wt. of Resin}}{\text{Cured Density of Resin}} + \frac{\text{Wt. of Nylon}}{\text{Density of Nylon}} + \frac{\text{Wt. of Microspheres}}{\text{Density of Microspheres}}$$

$$= \frac{\text{Wt. of Composite}}{\text{Density of Composite}} \neq 1$$

The ideal relationship assumes that no volume change occurs in the microspheres during processing, that ideal packing of the ingredients is obtained, and that no porosity occurs other than that deliberately added by the hollow microspheres. Also, it assumes that the resin flows, wets, fills all the interstices among the inert ingredients. The concept is shown schematically in Figure 30. It should be noted that to reduce the Langley formulation to unit size the microspheres must be crushed, and that even so, insufficient resin is present to fill all the interstices. Since both the nylon material and the final density are fixed quantities, it was decided that a mathematical approach would be fruitful.

Mathematical Analysis of Volume Fraction Relationships

For composites made up of phenolic (novolac) resin, phenolic microspheres, and nylon there are only four variables to consider if the nylon content is kept constant at 40 percent by weight. (Specifying a constant nylon content implies that density control is accomplished by interchange of phenolic resin binder with phenolic microsphere filler.) These four variables are:

1. Filler packing fraction.
2. Novolac weight fraction.
3. Microspheres density.
4. Fraction of microspheres crushed.

The novolac is the binder and if processing conditions are assumed to be such that melting and flow of the resin can occur before its gelation, then there are two cases to consider. The first case is that in

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HUGHES

1 UNIT VOLUME

NYLON

MICROBALLOONS

RESIN

LANGLEY
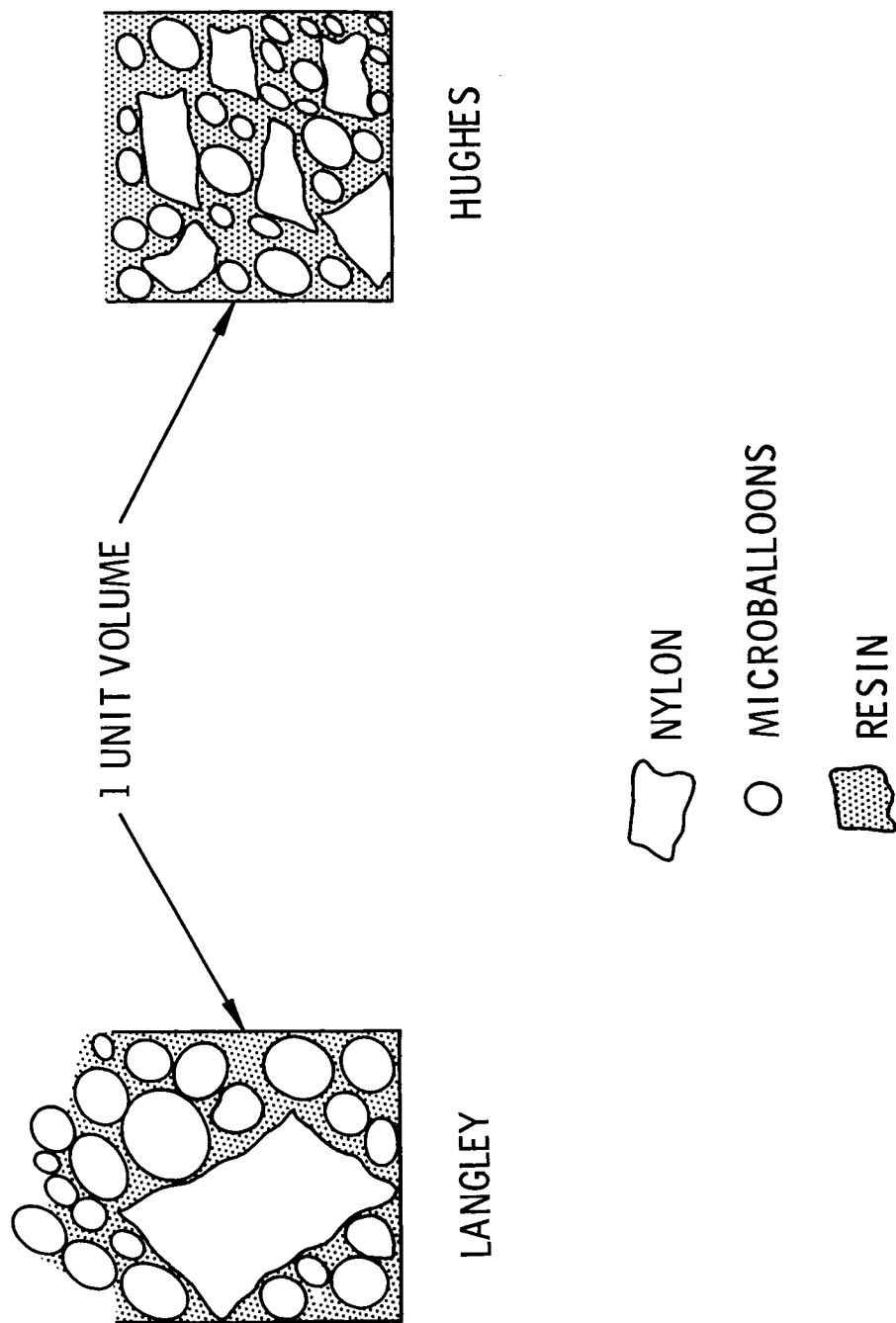
Figure 30. Diagrammatic representation of volume fraction relationships.

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which the material is so short of resin that regardless of the latter's fluidity and regardless of the pressure applied it cannot flow into and occupy all of the continuous void volume. Thus, there are always filler particles in contact with one another, and some continuous voids are present. In the second case, none of the filler particles are in contact, all being suspended in a continuous resin matrix.

Let

δ_i = density of ingredient, i

F_i = weight fraction of i

P = packing fraction of filler

$1 - P$ = volume fraction of continuous voids and resin

subscripts: i = 1, 2, 3, m

1 = phenolic resin

2 = microspheres

3 = nylon

m = mixture

By definition: $P = \dfrac{\delta_m F_2}{\delta_2} + \dfrac{\delta_m F_3}{\delta_3}$. We assume

$$F_3 = 0.4, \quad F_2 = 0.6 - x, \quad F_1 = x$$

x = variable resin weight fraction

Case 1

$$x\delta_m < \delta_1 (1 - P)$$

x_c, the critical value of x, at which we cease to have continuous voids and pass over to the second case is found from

$$x_c \delta'_m = \delta_1 (1 - P)$$

or

$$\delta'_m = \dfrac{P}{\dfrac{0.6 - x_c}{\delta_2} + \dfrac{0.4}{\delta_3}} = \dfrac{\delta_1 (1 - P)}{x_c}$$

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Thus composite densities can be calculated from

Case 1

$$\delta_m = \frac{P}{\frac{0.6 - x}{\delta_2} + \frac{0.4}{\delta_3}} \quad , \quad x < x_c$$

Case 2

$$\delta_m = \frac{1}{\frac{x}{\delta_1} + \frac{0.6 - x}{\delta_2} + \frac{0.4}{\delta_3}}, \quad x > x_c$$

It was decided to use the above relationships to estimate composite densities at two different filler packing fractions, viz. 0.74 and 0.50. The first corresponds to the theoretical closes packing of uniform spheres. The second value approximates the packing fraction of vibrated phenolic molding materials (commercial general purpose) before molding. Thus, the first represents a probably unattainable upper limit while the second is a realistic and attainable goal.

Assuming no crushing of microspheres (of density 16.5 lbs/cu ft) the effect of novolac fraction upon the cured material density is shown in Figure 31. The formulations worthy of experimental investigations can be approximated from this figure.

Actually the density of microspheres is not constant as implied by Figure 31. Allowance for the variability of this factor is made in Figure 32. This figure shows the formulations potentially capable of yielding the presently desired cured material density.

Figure 33 shows the formulation requirements for different cured material densities.

Figure 34 is the same as Figure 33 except that allowance is made for the crushing of microspheres.

Revised Formulation

On the basis of the relationships shown in Figures 31 through 34, it was possible, with minor assumptions, to select a formulation with the desired properties. Also, it was possible to adjust a given

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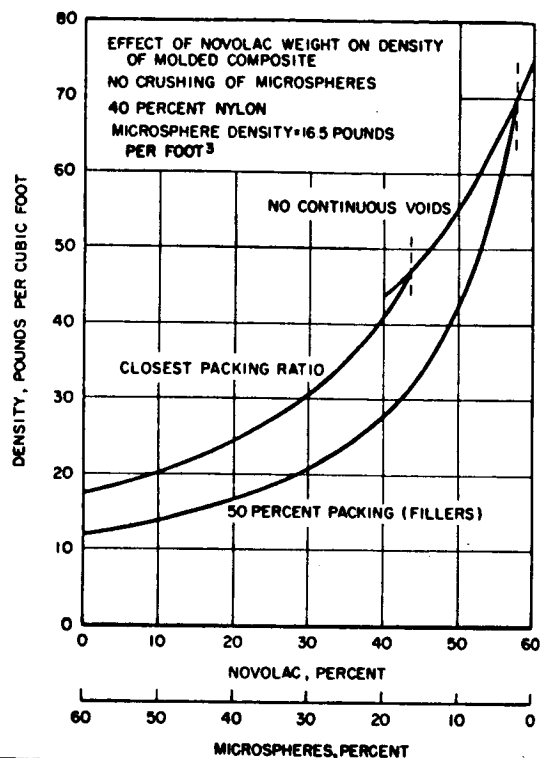
Figure 31. Effect of novolac weight on density of molded composites.
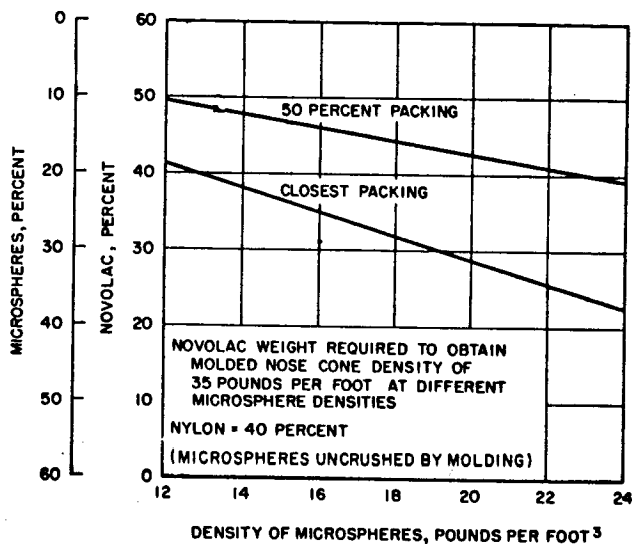
Figure 32. Novolac weight required to obtain molded composite density of 35 lbs/ft^3 at different microspheres densities.
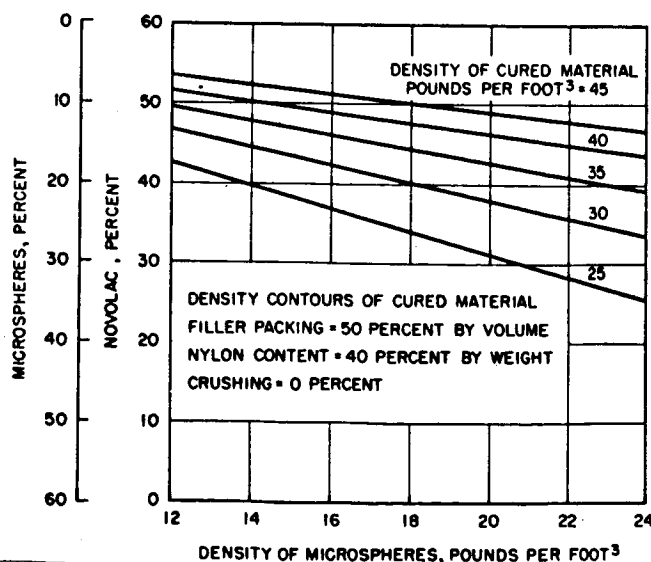
Figure 33. Density of cured material.
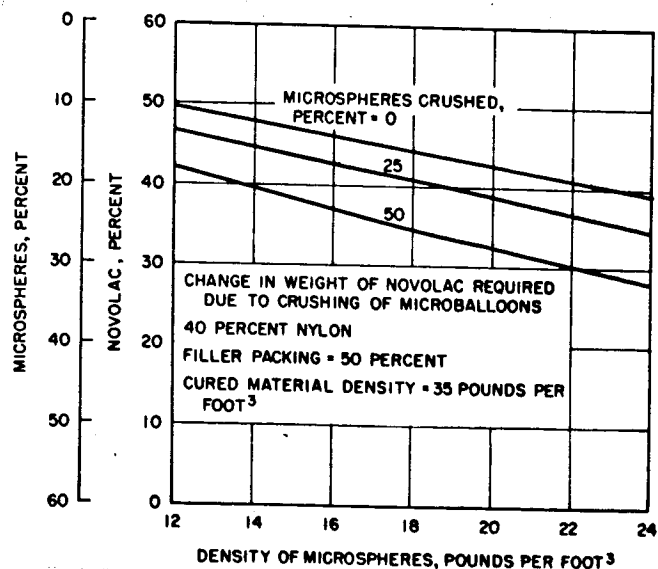
Figure 34. Change in weight of novolac required due to crushing of microspheres.

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formulation for variation in the true density of each batch of micro-
spheres. The formulation selected was designated Hughes LAF #1.
The LAF #1 formulation is contrasted with the Langley Molded Billet
Formulation in Table 48.

| Item | Hughes LAF #1 | | Langley | |
	Amount by Weight	Description	Amount by Weight	Description
Resin	37%	Hughes HFN Novolac	25%	Commercial Phenolic Novolac
Pneumagen	40%	Powdered Nylon 66 (-120 Mesh)	40%	Powdered Nylon 66 (80 Mesh Average)
Void Producers	23%	Upgraded Phenolic Microspheres (-50 + 230 Mesh)	35%	Phenolic Micro-spheres - as received

Table 48. Formulations for Hughes LAF #1 and
Langley molded billets

3.3 PROCESS MODIFICATION

Two major drawbacks were observed in receiving the Langley
Process. The application of an excessive and positive pressure to the
formulation during molding was part of the reason for damage to the
microspheres. Also, the heating of the formulation during cure solely
by heat transfer from the mold resulted in very high temperature dif-
ferentials within the billet and an extremely long cure cycle. The tem-
perature differential problem was magnified by the fact that the uncured
formulation is itself an excellent thermal insulator.

All of these conditions could be alleviated by two changes in the
molding. These changes were 1) molding to size, and 2) dielectrically
preheating. If the Scout Nosecap could be molded to size instead of
molding a massive billet the temperature differential problem would be
reduced because a much smaller volume of material would be cured at

one time. Also, a properly designed mold would have built in lands to absorb the press load once the mold had been closed. The mold would be close to a fixed volume. Provided the correct amount of material to achieve the desired density had been charged into the mold, the material would only be subjected to severe pressure during mold closing. Exact density control of the Nosecap would be achieved because the charge would be precisely weighed and the molded volume would be constant.

Dielectric pre-heating of the mold charge was considered to be desirable for several reasons. The elevated temperature produced by the preheating would be uniform throughout the mold charge, thus reducing the heat transfer problem. A correctly preheated charge would be semi-fluid and would therefore have much greater heat transfer capability than the cold powdered charge used in the Langley process. In addition, the fluid resin phase produced by the preheating would tend to protect the microspheres from damage during mold closing. Finally, the preheated material would be placed directly in a hot mold thereby eliminating the mold heat-up period and reducing the cure time.

3.3.1 Preliminary Molding Investigations

Several preliminary questions had to be answered before a decision would be made to change the process. Some of these questions were, 1) could the formulation be uniformly dielectrically preheated without overheating, charring, and too rapid cure? 2) Would a preheated charge molded in a hot fixed cavity volume mold be uniform in density? 3) Would this procedure reduce damage to the microspheres? and 4) Would a degree of flow occur during molding so that a shaped molding of uniform density would be achieved? Several small molding investigations were therefore initiated.

Three discs, nominally one inch thick and 3-1/2 inches in diameter, were molded from the following materials using the NASA Langley formulation proportions.

- Commercial Novolac from Batch No. C1020A
- 80 mesh Nylon 66, per NASA Specification
- Phenolic microspheres from Lot No. C505

The first disc was molded using an approximation of the NASA molding cycle. The second and third discs were molded by placing a dielectrically preheated charge directly into a 300°F mold and molding for 2 hours. The second disc was preheated for one minute at 200 ma while the third disc was preheated for 1.5 minutes at 200 ma.

The density variations through the three discs was studied by machining the ends and sides in a series of operations, weighing between each machining operation.

The density of the removed material as well as that remaining was calculated from the data. The results indicate the second disc molded from the dielectrically preheated material to be slightly more uniform than the disc molded using NASA conditions. The third disc which was preheated as much as possible was about as variable in density as the NASA disc. The results were sufficiently encouraging to support the belief that dielectric preheating and straight forward molding in a heated mold would produce uniform material. The results are tabulated in Table 49.

Additional molding studies were carried out using a 4 inch diameter mold fitted with vacuum and adjusted to provide a 1,000 inch deep cavity when closed to lands. Material was mixed from supplies of the commercial materials at Hughes using the Langley formulation. Two molding cycles were used, one approximating the Langley molding technique, and one using dielectric preheating and direct molding at cure temperature.

Preheated Molding Procedure

Dielectrically preheat charge, load directly in mold heated to 300° ±5°F. Level charge and place two bleeder plies of glass cloth (.020 inch thick total) on top of charge. Close mold rapidly with vacuum to lands using minimum press load. Cure 45 minutes at 300°F. Eject part hot.

Disc Number	Cut Number	Dia. In.	Thickness In.	Volume, Cu. In.	Wt. Gm.	Density of Remaining Mat'l, lb/cu ft	Density of Mat'l removed, lb/cu ft
1. (NASA Molding Cycle)	(Start)	3.475	0.993	9.418	94.00	38.00	-
	1	3.225	0.993	8.112	81.11	38.07	37.57
	2	3.225	0.870	7.107	70.80	37.93	39.06
	3	2.975	0.870	6.048	60.51	38.09	36.99
	4	2.975	0.746	5.186	51.58	37.87	39.44
	5	2.725	0.746	4.351	43.50	38.06	36.84
	6	2.725	0.618	3.604	35.80	37.82	39.27
	7	2.475	0.618	2.973	29.63	37.94	37.23
	8	2.475	0.495	2.381	23.80	38.05	37.51
	9	2.227	0.495	1.928	19.30	38.10	37.79
	10	2.227	0.372	1.449	14.32	37.62	39.57
	11	1.976	0.372	1.141	11.31	37.74	37.17
	12	1.976	0.248	0.760	7.42	37.16	38.94
2. (1.0 min. Diel. Preheat)	(Start)	3.483	0.993	9.461	92.39	37.18	-
	1	3.236	0.993	8.167	79.89	37.25	36.77
	2	3.236	0.868	7.139	69.63	37.13	38.00
	3	2.986	0.868	6.078	59.43	37.23	36.62
	4	2.986	0.744	5.210	50.63	37.00	38.58
	5	2.734	0.744	4.368	42.71	37.23	35.80
	6	2.734	0.618	3.628	35.39	37.14	37.67
	7	2.485	0.618	2.997	29.29	37.20	36.71
	8	2.485	0.492	2.386	23.43	37.38	36.51
	9	2.235	0.492	1.930	19.03	37.53	36.74
	10	2.235	0.369	1.448	14.16	37.23	38.42
	11	1.985	0.369	1.142	11.21	37.36	36.74
	12	1.985	0.240	0.743	7.21	36.97	38.14
3. (1.5 min. Diel. Preheat)	(Start)	3.483	0.992	9.452	93.21	37.55	-
	1	3.236	0.992	8.159	80.30	37.47	38.01
	2	3.236	0.869	7.147	70.50	37.55	36.88
	3	2.985	0.869	6.081	60.11	37.63	37.12
	4	2.985	0.745	5.214	51.57	37.66	37.47
	5	2.734	0.745	4.374	43.49	37.86	36.62
	6	2.734	0.622	3.652	36.38	37.93	37.49
	7	2.485	0.622	3.017	30.22	38.14	36.94
	8	2.485	0.495	2.401	24.19	38.36	37.27
	9	2.236	0.495	1.944	19.69	38.56	36.86
	10	2.236	0.372	1.461	14.72	38.37	39.18
	11	1.985	0.372	1.151	11.70	38.69	37.15
	12	1.985	0.246	0.761	7.67	38.35	39.35

Table 49. Density of molded discs.

Temperature Cycled Molding Procedure

Place cold charge directly in mold at 215° ±.005°F, level and add bleeder plies. Close mold with minimum pressure load to loads. Maintain 215°F temperature for 15 minutes. Raise mold temperature to 300° ±5°F in 45 minutes. Cure for 45 minutes at 300°F. Cool mold to 200°F before removing part (approximately 30 minutes).

Following molding and cooling in a desiccator the parts were machined on the top surface, and measured. Results are shown in Table 50.

Molding Procedure	Charge Wt gm	Av. Dia Inches	Av. Height* Inches	Weight gm	Density lbs/cu ft
A	112	3.9688	.9743	106.63	33.70
A	120	3.9691	.9610	112.69	36.10
A	130	3.9690	.9616	114.14	36.54
A	140	3.9685	.9702	134.70	42.75
B	112	3.9743	.9510	104.36	33.70
B	120	3.9738	.9658	114.28	36.35
B	130	3.9708	.9685	125.51	39.84
B	140	3.9705	.9645	133.72	42.65
*This dimension dependent on machining variables					

Table 50. Density of molded discs.

Some difficulties were encountered in establishing optimum preheat and loading the preheated charge in the mold without loss.

The investigation of the effect of dielectric preheating and the variation of density by changing mold charge weight was continued. The 4 inch dia x 1 inch disks were subjected to postcure in a helium atmosphere. The postcure schedule was as follows — Raise temperature rate of 5°F per hr from R.T. to 300°F, hold temperature at 300°F for 22 hrs, cool to R.T. in oven before removing parts.

The changes in density and volume of the disks after postcure are listed in Table 51.

Specimen Number	Mold Charge gm	Prior to Postcure			After Postcure		
		Density lbs/ft^3	Dia. Inches	Height Inches	Density lbs/ft^3	Dia. Inches	Height Inches
Langley Process							
A1	90	26.9	3.976	.958	27.0	3.970	.959
A2	100	29.9	3.976	.950	30.0	3.969	.950
A3	118	37.0	3.975	.950	37.1	3.960	.940
A4	125	38.1	3.968	.952	38.0	3.943	.949
Hughes Process (Preheated)							
B1	90	27.1	3.970	.957	27.1	3.964	.958
B2	100	30.4	3.970	.966	30.1	3.960	.964
B3	110	33.6	3.970	.964	33.5	3.952	.961
B4	115	35.4	3.965	.962	35.1	3.946	.959
B5	120	35.9	3.965	.962	35.7	3.947	.969
B6	130	40.1	3.962	.961	39.9	3.948	.959
B7	140	43.2	3.960	.962	42.9	3.950	.962

Table 51. Effect of postcure on density and dimensions of 4 inch dia by 1 inch disks.

A cursory examination of this data shows that a slight decrease in density occurs during postcure and that this effect is greater as the density increases. Also, additional shrinkage occurs during postcure and that the shrinkage in the diameter is more pronounced than in the height. This lower shrinkage in the height direction is to be expected because this is the direction of pressing. In almost all plastics a certain amount of unmolding occurs in the pressing direction which offsets the shrinkage.

The work on molding 4" diameter by 1" high disks with and without dielectric preheating was repeated with more accuracy. A large range of densities was obtained by varying the mold charge into the fixed volume of the mold. As anticipated no major difference in density was obtained by the method of processing. All of the billets molded were uniform in appearance and contained no visible faults. The results are plotted in Figure 35.

The primary significance of this data was that a simple molding procedure utilizing dielectric preheating and a total of 45 minutes molding time produce the same densities of molded material as a complicated heating and cooling procedure requiring over two hours molding time.

3.3.2 The Scout Nosecap Compression Mold

The preliminary molding investigations indicated that dielectric pre-heating and molding to size were feasible. A mold was therefore designed and fabricated (see Figure 36).

The mold was steam heated and had provision for evacuating air from the cavity. The cavity and force of the mold were made from pre-hardened tool steel, polished, and hard chrome plated.
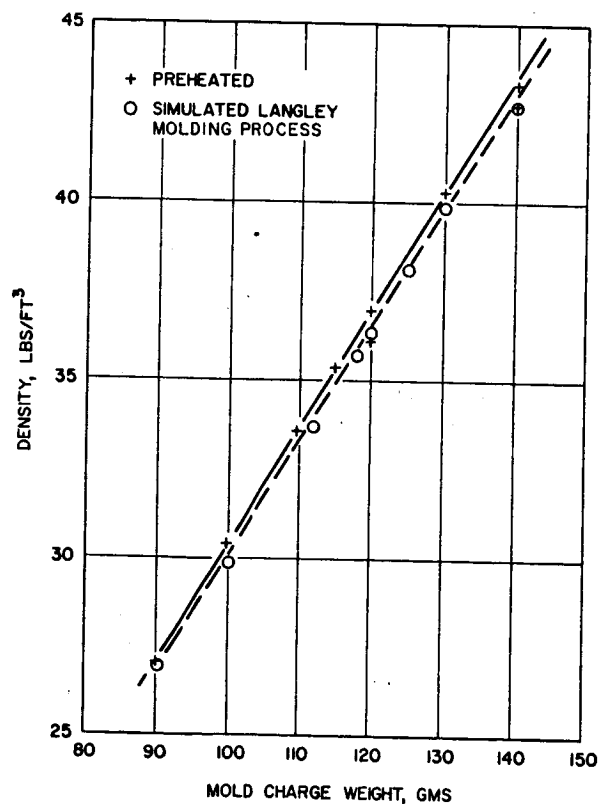
Figure 35. Mold charge versus molded density.

The large loading chamber and steam chamber were designed to be made from inexpensive steel tubing. Thermocouples were included in the mold but no pressure transducers because it was doubtful if the readings are meaningful.

The mold was designed to mold the nosecap directly to size using a dielectrically pre-heated charge. The weight of the charge was to be adjusted to completely fill the cavity with a very slight excess for flash. Since the mold closed to lands, pressure on the molding would only be a variable during the closing cycle or if an excess charge is used. It was planned to mold the cap without temperature cycling and to eject the molding hot. Shrinkage factors were placed on the mold dimensions as established from smaller moldings.

3.3.3 Preliminary Nosecap Molding

The Scout Nosecap mold was proved without difficulty. No trouble was experienced in mechanical operation, heating, and application of vacuum. Dimensions of the initial moldings appeared to be satisfactory. Several parts were molded from general purpose phenolic in order to break in the mold.

Nosecaps were then molded using the Langley formulation made from as received raw materials. No attempt was made to control moisture content and to assure optimum mixing of the formulation. By using two 4 KW dielectric pre-heaters and dividing the mold charges, several parts were made. These parts had good appearance and were of nominal 35 lbs/ft^3 density. However it was obvious that dielectric pre-heating capacity was marginal since several minutes were required to raise the temperature of the mold charge. Optimum pre-heat should have taken less than 60 seconds because of the short gel time of the resin.

A batch of Langley formulation was then prepared from pre-dried materials. Great care was taken to uniformly and intimately mix the constituents. Attempts to mold the batch were unsuccessful because of pre-heating difficulties. Parts of the mold charge were overheated and other portions were too cold. The moldings showed charred areas and a large variation in density. The formulation was then exposed to

Figure 36. Mold design - compression mold - scout nosecaps.

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humidity in order to increase flow and dielectric loss (and thus accelerate pre-heating) but unsatisfactory moldings were still obtained. It was therefore decided to rent a dielectric pre-heater of 12 KW capacity capable of pre-heating the entire mold charge in approximately 30 seconds.

In order to determine whether there was any major difference in physical structure between the Langley Billet material, gas transmission tests were performed on 3" diameter disks cut from the first molded nose caps. The test was performed by pulling a vacuum on one side of the disk and measuring the air flow through the disk with a gas burrette. Results are shown in Table 52.

These results showed that a significant change in physical structure had been achieved by the Hughes Molding Process and a formal molding study was therefore initiated.

Material	Density Lbs/Ft^3	Orifice Size Dia- inches	Disk Thick- ness Inches	Air Flow	
				Vol, ccs	Time, Mins.
Langley Billet #2	33.4	2.750	.250	Too large to measure	
		0.750	.250	Too large to measure	
		0.075	.250	Too large to measure	
Molded Nosecap Langley Formulation	37.5	2.750	.350	0	280
		2.750	.190	1	15
				2	25
				3	35
				4	46
				5	58
				6	73

Table 52. Gas transmission of preliminary molded nosecaps.

3.3.4 The Molding Program

The first experiments on direct molding of nosecaps were conducted on the standard Langley formulation. Due to the limitations of time and material it was not possible to completely optimize the process. However, it was attempted to bring the density variation within ± 5% of average.

It was found that preheated material could be adequately cured in the mold with a cure time of 90 minutes at 275°F. No blistering or evidence of undercure was observed with these curing parameters. Cure was completed by postcuring to 350° ± 10°F for 6 hours in an argon atmosphere.

The most critical parameter in controlling density variations was found to be the size and shape of the preform. Simple disk shaped preforms were found to give high density in the center of the molding.

Five formulations were selected for the molding of Nosecaps and delivery to various agencies for evaluation as shown in Table 53.

The five formulations were designed to provide specimens for test which would represent the difference between the Langley and LAF #1 formulations with and without upgraded nylon and microspheres. The Formulation Number 5 represented all of the Hughes innovations including the Hughes process, upgraded nylon and microspheres, and the HFN phenolic novolac. The primary effort was expended on Formulation Number 5. The experimental plan for the molding program is shown in Appendix VI.

Formulation No. and Description	Ames	Langley	Stanford Research Institute	Langley (Scout Proj. Office)
1. Hughes Molding Process Langley Formulation Commercial Resin Ungraded Materials 25% Commercial Resin 40% Nylon 35% Microspheres	2	1		

Table 53. Nosecap formulation and deliveries.

Formulation No. and Description	Ames	Langley	Stanford Research Institute	Langley (Scout Proj. Office)
2. Hughes Molding Process Hughes Formulation Commercial Resin Ungraded Materials 37% Commercial Resin 40% Nylon 23% Microspheres	2	1		
3. Hughes Molding Process Langley Formulation Commercial Resin Upgraded Nylon (-120 mesh) Upgraded Microspheres 25% Commercial Resin 40% Nylon 35% Microspheres	2	1		
4. Hughes Molding Process Hughes Formulation Commercial Resin Upgraded Nylon (-120 mesh) Upgraded Microspheres 37% Commercial Resin 40% Nylon 23% Microspheres	2	1		
5. Hughes Molding Process Hughes Formulation New Resin Upgraded Materials 37% HFN Resin 40% Nylon 23% Microspheres	2	2	5	5

Table 53 (continued). Nosecap formulation and deliveries.

= Drying of Materials

Low temperature drying of Nylon, microspheres, and novolac, was investigated. The effect of removing moisture by drying for 8 hours at $120^{\circ}F$ was found to stiffen and decrease the flow of the molding formulation to a noticeable degree. It was therefore decided to adjust the formulation to account for the volatile materials and to use undried materials.

Formulation of all batches was carried out as described in the Molding Program. Sieved Microspheres were used in the "upgraded" formulations. Undried raw materials were used with each formulation corrected for moisture content of the ingredients. It was also found that greater homogeneity was achieved when the formulation for each molding was tumbled for ten minutes immediately before molding and then passed through a 50 mesh sieve. This treatment eliminated any tendency for the ingredients to segregate and agglomerate. The -120 mesh Nylon had a strong tendency to do this. The barrel tumbler provided adequate mixing for batches as large as 10,000 gm. The formulation was not damaged by tumbling for long periods (up to 16 hours) since the mixing action was gentle.

Preforming and Preheating

During the first attempts to mold the Langley Formulation it was recognized that a simple disk shaped preform of even thickness would not produce a nose cap of even density. The formulations compress in the direction of pressing but do not transmit the pressure laterally to a large extent. Therefore only a small amount of lateral flow occurs in the mold. The problem was complicated by the fact that a large portion of the material in the nose cap was at the edge and the material cannot be expected to flow from the center of uniformly thick preforms to fill out the edges.

The first moldings therefore made with a uniformly thick preform were therefore dense in the center compared to the edge. Variation of density from 40-45 lb/ft^3 in the frontal area of the cone to 23.28 lbs/ft^3 in the skirt was found as anticipated.

A preform container was therefore constructed which permitted a concentration of material in the edge rather than the center of the preform. The preform mold was vacuum formed from 1/16 inch thick polypropylene sheet to form a low loss container which did not interfere with preheating. The cup shaped preform (Figure 37) was used in the inverted position in the dielectric preheater. After preheating the preheated formulation readily separated from the preform container and retained its shape while being turned over and placed in the compression mold.

Although the cup shaped preform permitted the dielectric preheating of the entire mold charge in one operation it had two disadvantages. First the dimension A (Figure 37) had to be varied according to the bulk factor of each formulation in order to obtain the correct proportions of material in the edge and center of the molding. Second, the difference in thickness of the center and edge of preform prevented uniform preheating. In order to overcome this problem two preforms, a disk and a ring, were made. (Figure 38). These would be uniformly loaded and the relative amount of material in each preform could be adjusted to give precise density control in the finished part. The preforms could each be separately preheated to optimum condition and assembled for placement into the mold. No evidence of an internal weld at the preform juncture could be found in the finished moldings provided preheating conditions were correct. The juncture between the preforms could be discerned on the interior surface of the moldings but was evidently only a surface effect and should not affect the performance of the part. The two-preform technique was therefore adopted for all of the Formulation 5 (Hughes Formulation, HFN Resin, Upgraded Nylon and Microspheres) nosecaps.

Molding to Size

The compression molding of properly preheated preforms proved to be straightforward. Preheating conditions were generally 35-60 seconds with a final plate amperage reading of 1.2 amps. The preform or preforms were removed from the preform containers and transferred
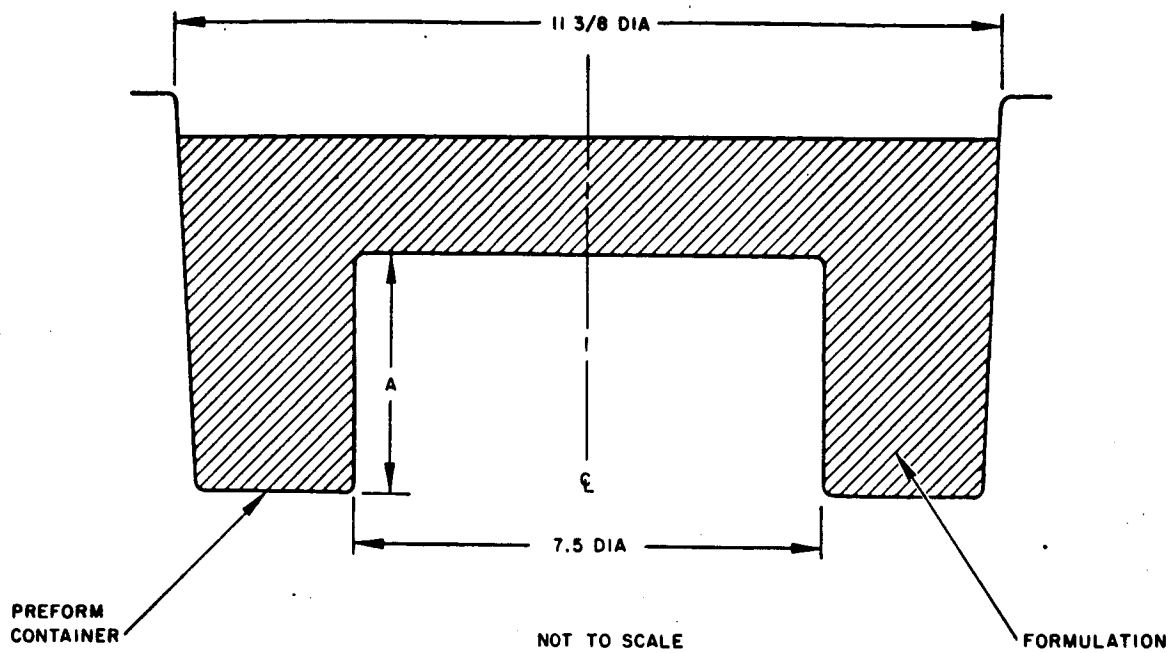
Figure 37. Cup shaped preform container.

to the hot mold in 20-30 seconds. The mold was closed slowly (approx. 50 seconds) to full pressure and the parts cured for 90 minutes at 275 $\pm$ 5°F and removed hot. The total press cycle per molding was 100 minutes including mold preparation and cleanup. No problems were encountered in postcure.

Overall density control of the moldings was excellent. A standard mold charge, based on the volume of the molding, of 1785 gm was used. Molded parts varied from 1735 to 1765 gm. After postcure the parts ranged from 1700-1730 gm. The calculated weight of the parts to achieve 35 lbs/ft^3 was 1710 gm.

The variation of density within the nose caps was not controlled to optimum because of the limited time and material. The process, however, especially the two preform method was amenable to very close control and adjustment. Density control close to $\pm$ 5% of 35 lbs/ft^3 was achieved. Slight adjustment of the weight and shape of the preforms will reduce this variation to possibly 35 $\pm$ 0.5 lb/ft^3 throughout the nose cap.

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RING PREFORM CONTAINER

DISK PREFORM CONTAINER
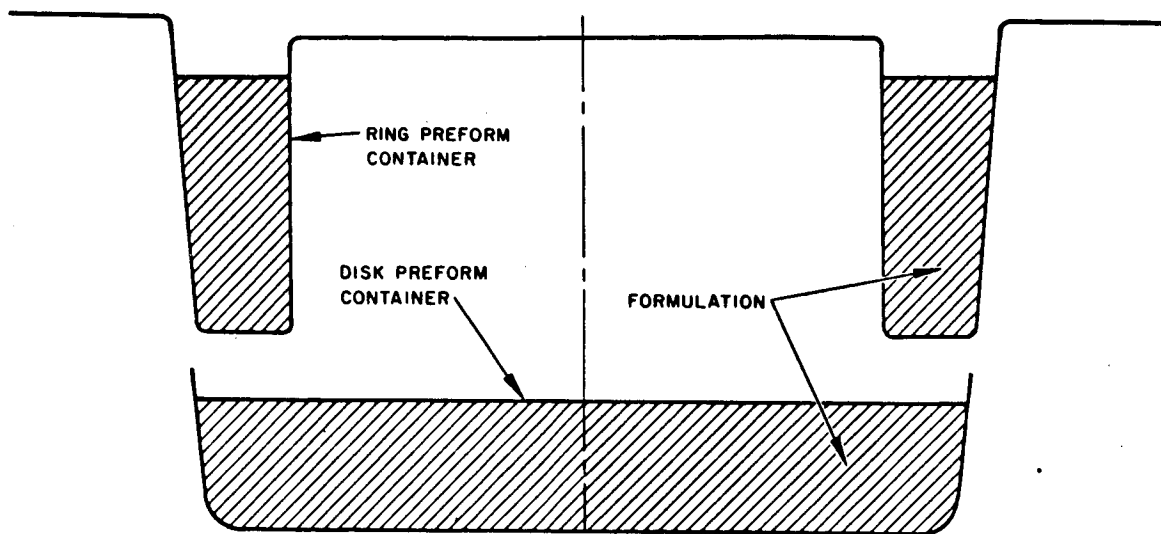
FORMULATION

NOT TO SCALE

Figure 38.   Ring and disc shaped preform container.

The molding conditions used for each formulation are listed in Table 54.

Density Variations

The sampling technique and variation of density throughout the molded caps is shown in Figures 39 and 40.   A .750 dia x 1. 132 long cylindrical density specimen was taken from each of the five radial stations as shown.   In general a high density area was found at the edge or transition area of the caps.   However, it must be reiterated that the process was amenable to refinement and the minor changes in preform weight and shape can bring the density within finer tolerances.   Typical density versus location plots are shown in Figure 40 for individual nose caps of each of the five formulations molded.   The density specimens were taken immediately after molding.   The postcured density of the specimens was 2-3 percent lower than the figures shown.

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Formulation	Type of Preform	Preform Weight gm	Preheat Time to 1.2 Amps Seconds	Mold Closing Time Seconds	Press Load Tons	Mold Temp. °F	Cure Time Mins.	Molded Wt gm	Postcured Wt gm
Item 1 - Langley Formulation 25% Commercial Resin 40% Powdered Nylon 80 Mesh 35% Ungraded Phenolic Microspheres	Cup	1785	50	30	150	275±5	90	1753	1730
Item 2 - Hughes Formulation 37% Commercial Resin 40% Powdered Nylon 80 Mesh 23% Ungraded Phenolic Microspheres	Cup	1785	60	50	150	275±5	90	1758	1725
Item 3 - Langley Formulation Upgraded 25% Commercial Resin 40% Powdered Nylon -120 Mesh 35% Sieved Microspheres (-50, + 230 Mesh)	Cup	1785	55	30	150	275±5	90	1739	1703
Item 4 - Hughes Formulation Upgraded 37% Commercial Resin 40% Powdered Nylon -120 Mesh 23% Sieved Microspheres (-50, + 230 Mesh)	Ring and Disk	1385 400	50 100	25	150	275±5	90	1759	1720
Item 5 - Hughes Optimum Formulation 37% Hughes HFN Novolac Resin 40% Powdered Nylon -120 Mesh 35% Sieved Microspheres (-50, + 230 Mesh)	Ring and Disk	928 857	55 60	25	150	275±5	90	1744	1705

Table 54.   Final molding conditions for Scout nosecap formulations

STATION NO. 1

STATION NO. 2

STATION NO. 3

STATION NO. 4

STATION NO. 5

~2

~2

~1 1/2

~1 1/2

ALL DIMENSIONS IN INCHES

DENSITY SPECIMENS 0.750 DIA x 1.132 HIGH CYLINDERS
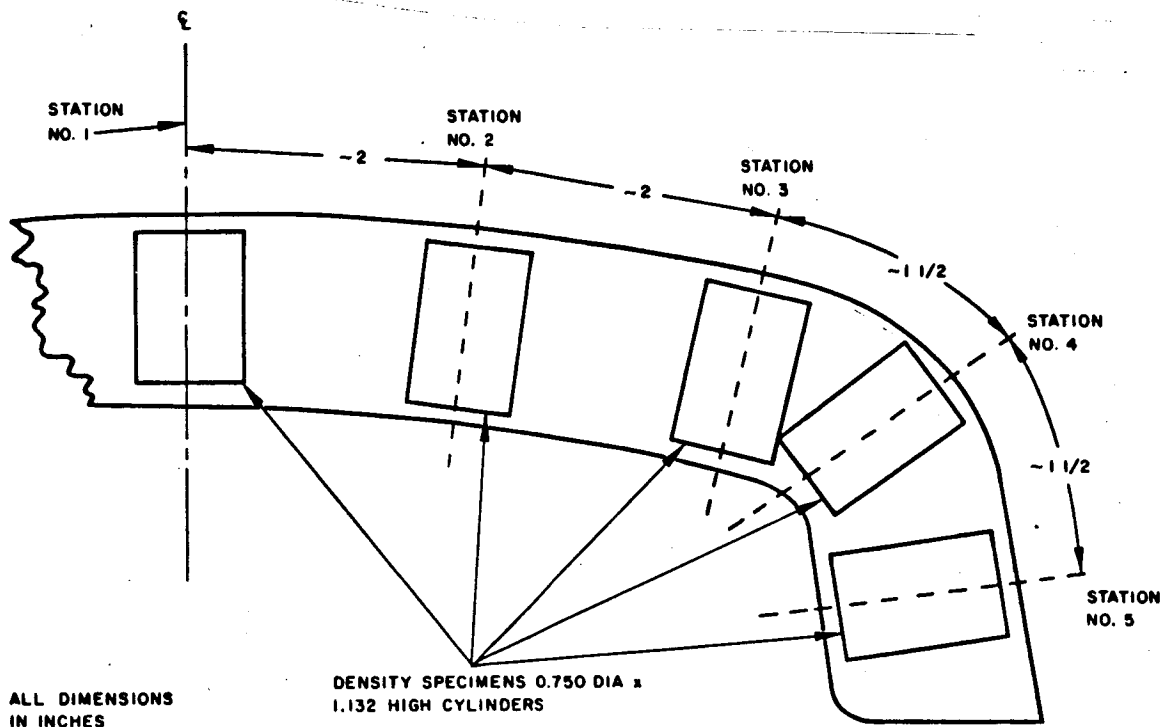
Figure 39. Location of density specimens in molded Scout nosecaps.

In addition to the capability of molding large shapes by the use of multiple preforms, the process also offers another interesting potential. Nosecaps could be molded in which density variation was deliberately built in. High density material could be produced in critical high shear and turbulent areas to insure highest performance and lowest weight, modified formulations could be used in the various preforms, that is, areas of planned high density would utilize higher resin content and lower microsphere content than low density areas. Such formulations can readily be formulated using the principles already developed in this program.

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ITEM 5

HUGHES FORMULATION
37% HFN RESIN
40% -120 MESH NYLON
23% SIEVED MICROSPHERES

(PART NO. - 44A)

ITEM 4

HUGHES FORMULATION
37% COMMERCIAL RESIN
40% -120 MESH NYLON
23% SIEVED MICROSPHERES

(PART NO. 2H-3)

ITEM 3

LANGLEY FORMULATION
25% COMMERCIAL RESIN
40% -120 MESH NYLON
35% SIEVED MICROSPHERES

(PART NO. 2L-6)

(PART NO. I-H-14)

ITEM 2

HUGHES FORMULATION
37% COMMERCIAL RESIN
40% 80 MESH NYLON
23% UNGRADED MICROSPHERES

ITEM 1

LANGLEY FORMULATION
25% COMMERCIAL RESIN
40% 80 MESH NYLON
35% UNGRADED MICROSPHERES

(PART NO. I-L-15)

DENSITY, LBS/FT³

NO. I CENTER   NO. 2   NO. 3   NO. 4   NO. 5   EDGE

STATION NUMBER, LOCATION OF SPECIMEN

Figure 40.   Density vs location - molded nosecaps.

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3.3.5 Summary of the Final Production Process

The final formulation for 35-lb/ft^3 density material developed by Hughes is as follows:

37 percent by weight of Hughes HFN Phenolic Novolac (a highly characterized and pure analog of the commercial novalac)

23 percent by weight of graded Phenolic Microspheres. (That fraction passed by a 50 mesh sieve and retained on a 230 mesh sieve.)

40 percent by weight of Nylon 66 (-120 mesh)

The Hughes formulation was prepared by first determining the moisture content of the materials. Unless the moisture content was excessive, the materials were not dried because the moisture increases the flow and wetting ability of the resin. The correct proportio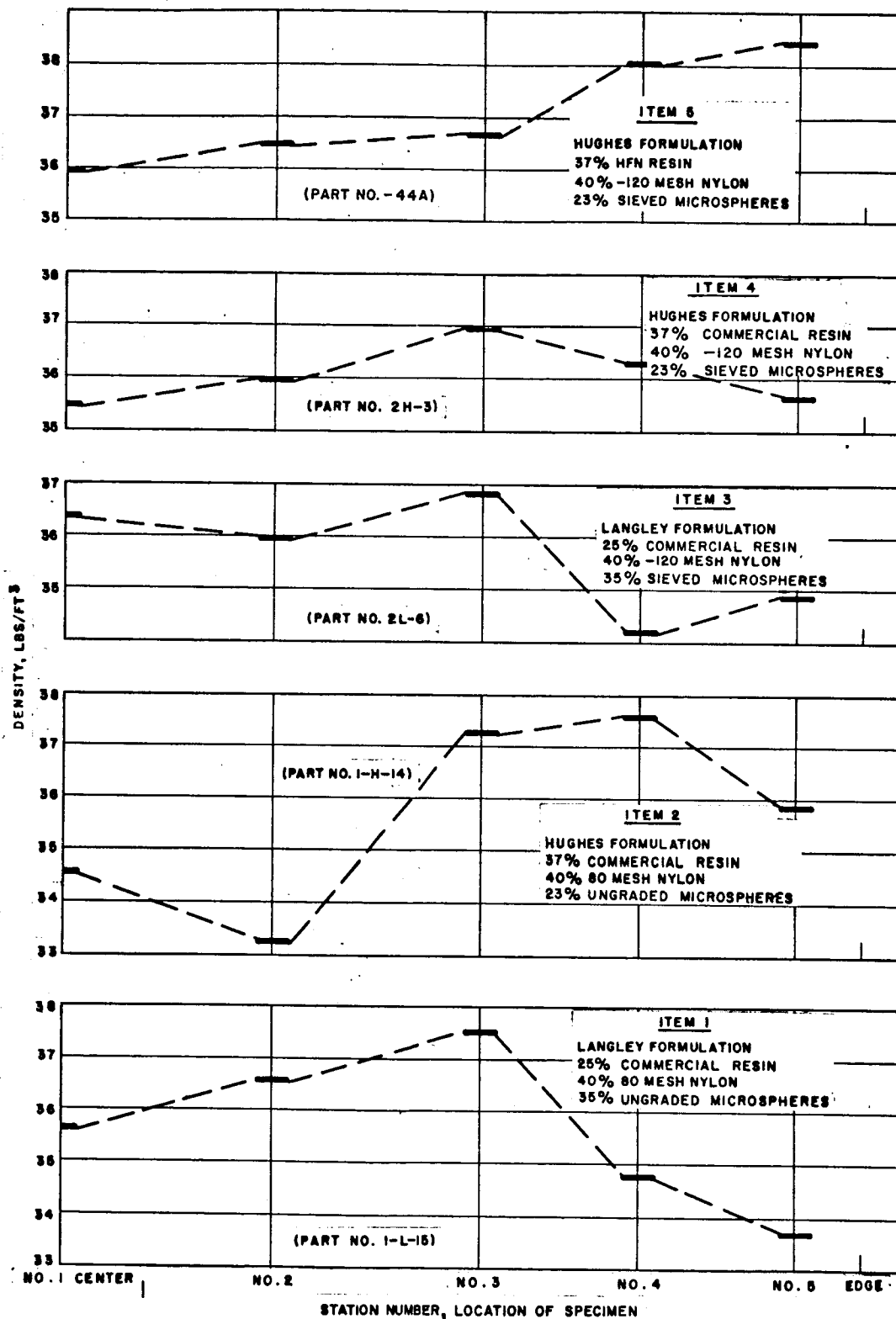ns of the ingredients, adjusted for moisture content, were then carefully weighed and dry blended in a similar manner to the Langley process.

To mold the Scout Nosecap to size two preforms were required. The nose portion of the cap was obtained by using an essentially disk shaped preform and the skirt of the cap was formed from a hollow cylindrically shaped preform. The preforms were produced by weighing a predetermined amount of blended formulation into vacuum formed polypropylene preform molds, Figures 41 and 42. The charge in each preform mold was then carefully smoothed on the surface to assure uniform distribution (Figure 43). The preforms were then dielectrically preheated for approximately 35 seconds in a 12 KW dieelectric preheater (Figures 44 and 45). The ring preform was then placed on the disk preform (Figure 46) and placed in the hot compression mold. The mold (Figure 47) was of the landed type and therefore always closes to a fixed cavity volume. Provided the correct weight of formulation was placed in the mold, the molding was always of the correct average density.

The nosecap was cured in the compression mold for 90 minutes at 275°F ± 5°F and then removed hot by using a suction cup (Figure 48). The part was then placed on a chill fixture (Figure 49) and insulated
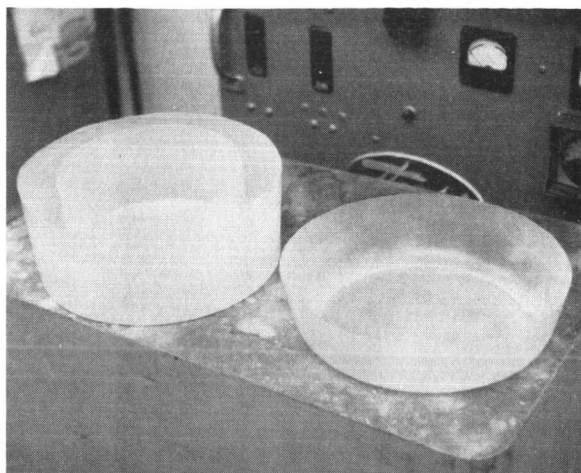
Figure 41. Ring and disk preform molds made of vacuum formed polypropylene sheet.
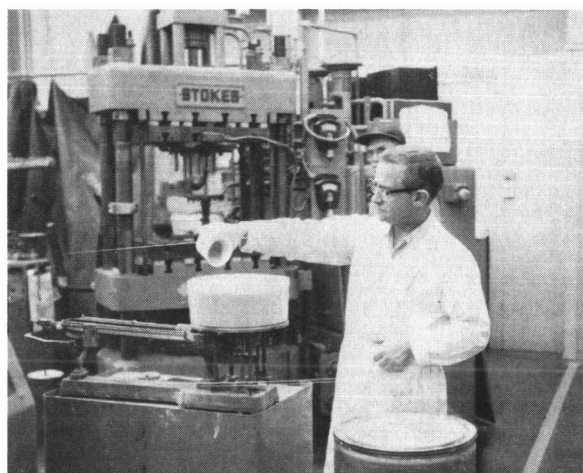
Figure 42. Weighing of Hughes formulation into ring preform mold.
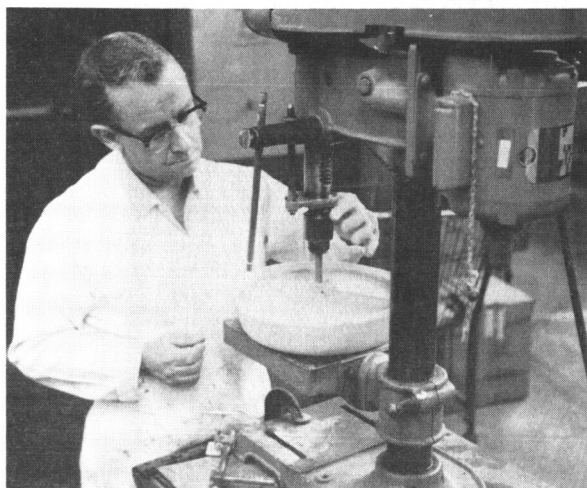
Figure 43. Smoothing of preform charge to assure uniform distribution of material.
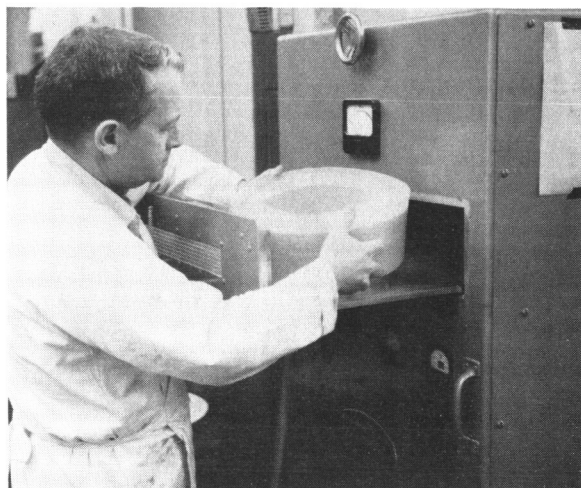
Figure 44. Dielectric preheating of preform.
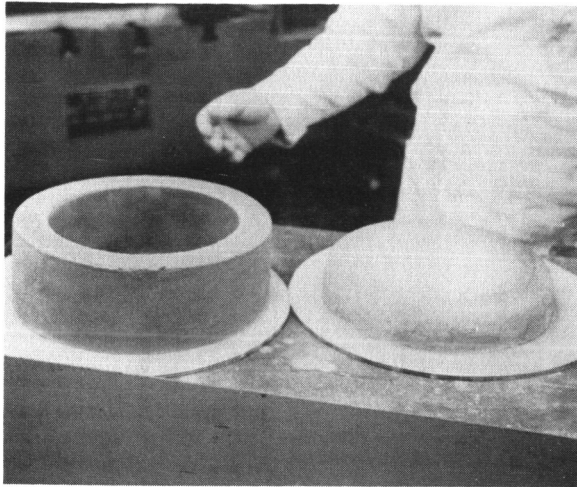
Figure 45. Preheated preforms, removed from preform molds prior to loading in compression mold.
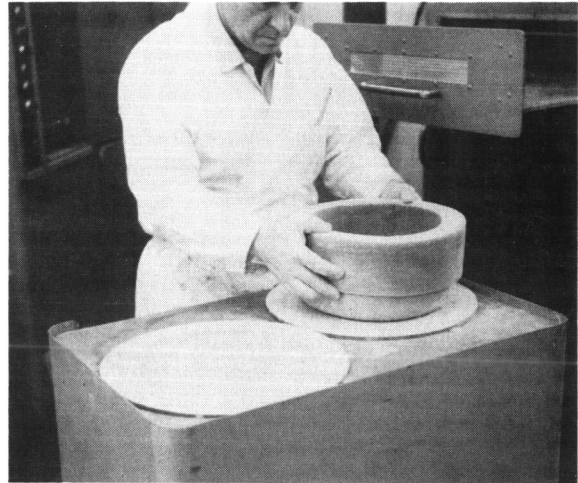
Figure 46. Assembly of preheated preforms for loading in mold.
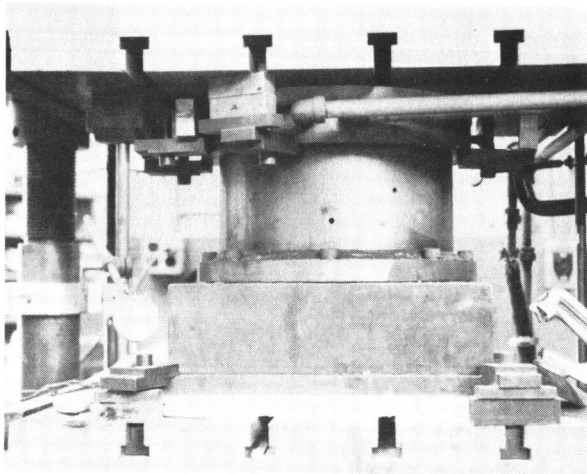
Figure 47. Closed compression mold for molding Scout nosecap to size.
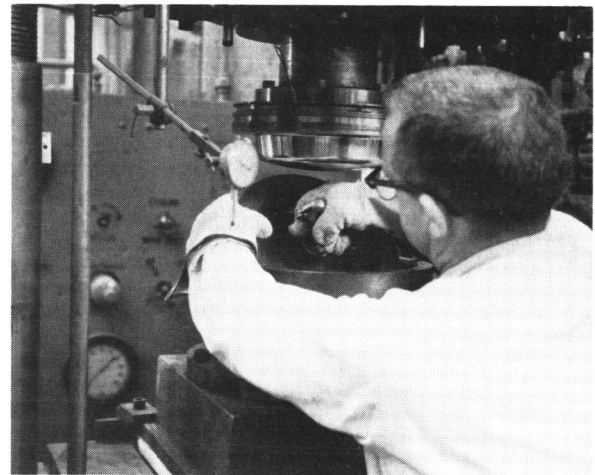
Figure 48. Removal of molded nose-cap from compression mold.

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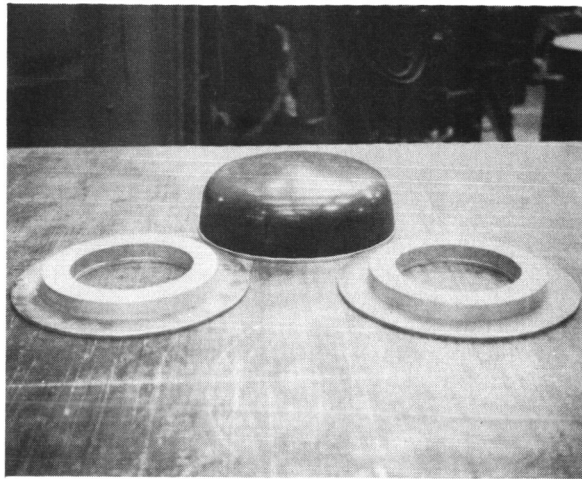
Figure 49.   Molded nosecap and shrink-
postcure fixtures.

Figure 50.   Postcured nosecaps
mounted in postcure
fixture.

with glass cloth to allow it to cool slowly. The total molding cycle for molding nose caps was 100 minutes.

The molded caps were post-cured while still on their shrink fixtures on the rack shown in Figure 50. The rack was placed in a sealed steel container. A continuous flow of argon gas was maintained through the post-cure canister during post-cure in a hot air circulating oven. The post-cure consists of a 24 hour cycle in which the temperature was raised to $350^{\circ} \pm 10^{\circ}F$ in 10 hours, maintained at $350^{\circ}F$ for 4 hours, and cooled for 4 hours.

3.4 CHARACTERIZATION OF MOLDED NOSECAPS

Compression strength, porosity (Hughes Method) and gas transmission tests were performed on the molded nosecaps. It should be noted that the compression strength of all nosecaps made, including those based on the Langley formulation was markedly increased by the Hughes molding process. Results are shown in Table 55.

Gas Transmission Test

In order to obtain a reproducible gas transmission test and to reduce the overriding effect of small flaws in the samples, transmission was measured by passing air at one atmosphere lengthwise through a .750 dia x 1.132 long cylindrical specimen. The results showed that this was a good control test for the Hughes product but that the Langley material was still so porous that gas transmission was limited by the flow capacity of the apparatus. (See Table 56.)

Porosity Tests

The data on interconnected and total porosity is too voluminous to present here. In summary however, the final Hughes Nosecaps showed significantly reduced continuous porosity compared to the Langley Material. (See Table 57.)

Description	No. Samples	Average Compression Strength PSI	Standard Deviation
Langley Billets			
Billet No. 2	57	2435	± 253
Billet No. 8	57	2575	± 318
Billet No. 12	18	2820	± 173
Average Langley Moldings		2610	
Hughes Molded Nose Caps			
Part No. 1L14, Formulation #1 (Langley Formulation un-graded raw materials)	4	3361	± 710
Part No. 1H13, Formulation #2 (Hughes Formulation ungraded raw materials)	3	3957	± 755
Part No. 2L5 Formulation #3 (Langley Formulation ungraded raw materials)	12	4128	± 375
Part No. 2H-1, Formulation #4 (Hughes Formulation upgraded raw material)	5	5107*	± 560
Part No. 3H-41, Formulation #5 (Hughes Formulation, upgraded raw materials, HFN resin)	5	3795	725
Part No. 3H-44A	5	4460	± 475
Part No. 3H-46	5	3773	± 560
Part No. 3H-49	5	3932	± 835
Part No. 3H-50	10	4870	± 1460
Average of Formulation #5 Moldings		4166	

*These specimens averaged 38.02 lbs/ft^3 density which probably accounts for the high compressive strength.

Table 55.   Compressive strength of molded nosecaps.

The porosity as measured by Aminco porosimeter confirmed the above data.   Specimen taken from the Langley Billets were compared with the Hughes LAF nosecap material.   The volume percent of mercury penetration as various pressures are listed in Table 58.

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Sample	Volume of Air Transmitted at Atmospheric Pressure	
	Time-Minutes	Vol in ml
#3H-50 Formulation #5 (Hughes, Upgraded, LFN Resin)		
Position #1	2	0.0
	30	0.0
Position #5	2	0.6
	5	1.3
	10	2.9
	15	5.4
	30	11.0
Position #2B	2	4.0
	5	15.3
	10	37.0
	15	55.1
	20	75.2
Position #2C	2	0.0
	5	0.3
	10	0.9
	15	1.3
	40	6.0
	60	9.0
	95	13.0
Position #2D	2	2.6
	5	5.2
	10	11.0
	15	17.3
	40	64.6
Langley Billet #8		
Specimen 1	43 Seconds	90.0*
Specimen 2	44 Seconds	90.0
Specimen 3	44 Seconds	91.0
*Transmission limited by size of orifice		

Table 56. Gas transmission of molded nosecaps.

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	Total Voids as % of Total Sample Volume	Volume % of Total Voids Which is Continuous (interconnected)
Langley	54% Average	68-70%
Hughes (upgraded LFN Resin)	52% Average	15-20%

Table 57. Porosity as measured by epoxide impregnation.

Hg Volume Penetration, %

Pressure, psi	Langley Billet	Hughes LAF Formulation
15	1.7	2.8
30	24.1	12.1
45	28.3	14.0
60	30.1	14.7
300	33.9	15.8

Table 58. Porosity-Determination Aminco-Winslow porosimeter.

From the data it is apparent that the continuous voids occupy a lower percentage of the total volume and the discrete voids have a larger volume in the Hughes formulation. Figures 51 and 52 show the difference in porosity of the two materials.

Tensile Tests

The tensile strength of the Formulation Number 5 nosecap material was measured on the dogbone specimen described previously in the Langley billet characterization. The results are shown in Table 59.

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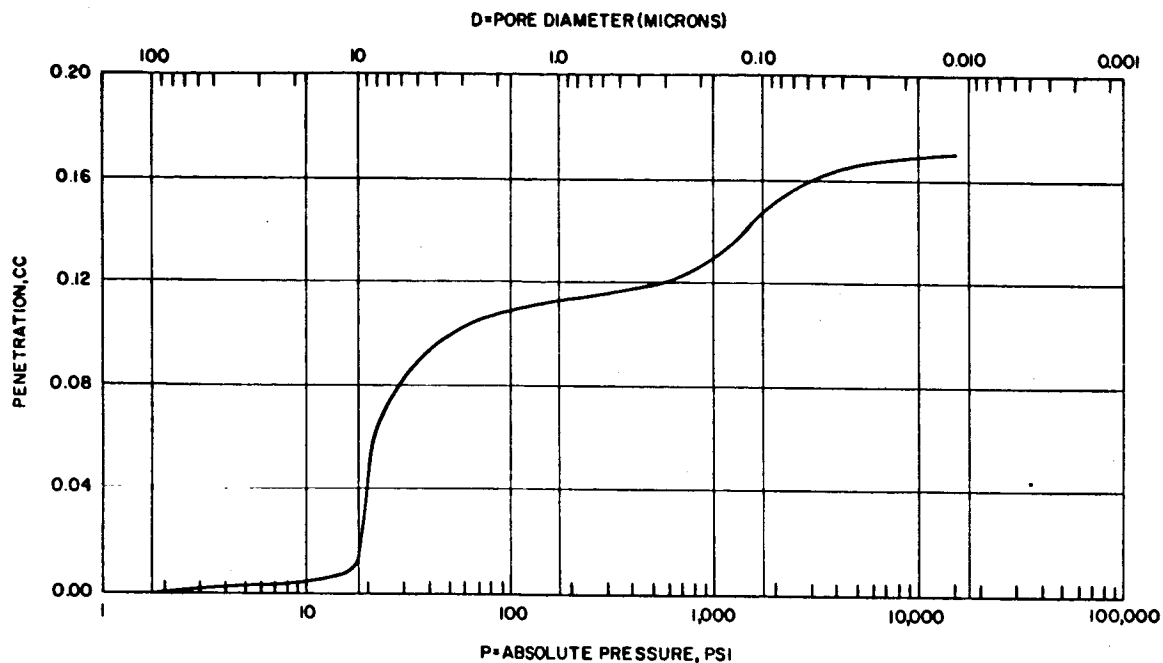
Figure 51. Aminco-Winslow porosimeter determination
Langley billets.
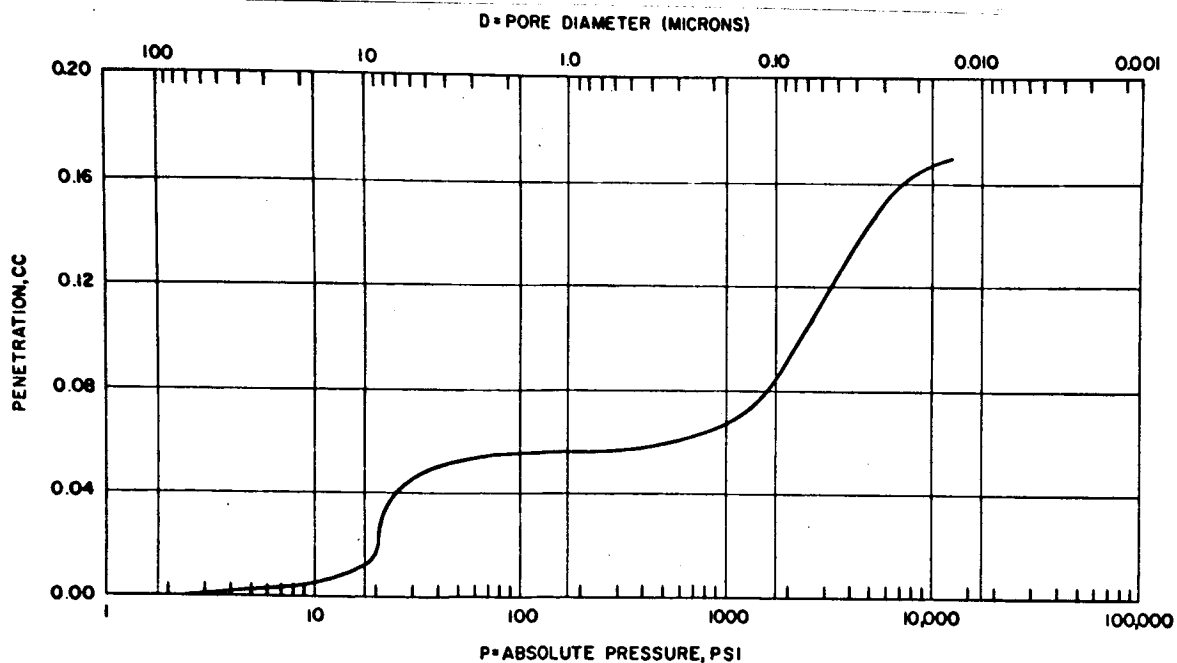
Figure 52. Aminco-Winslow porosimeter determination
Hughes LAF nosecap.

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Molded Nosecap Number	Tensile Strength-psi
3H35	1103
3H35	1250
3H36A	1220
3H36A	1345
3H40	1455
3H41	1290
3H44A	1500
3H46	1304
3H53C	1273
3H53E	1384
	Mean 1312.4 Std. Dev. ±115.5

Table 59. Tensile strength of formulation #5 nosecap.

Appearance and Photomicrography

Specimens cut from the Highes molded Nosecap exhibited a much finer and more uniform grain structure than those cut from Langley billets. The material was less friable, and machined in a cleaner manner with less chipping and crumbling at the tool bit. The cut surfaces of postcured specimens were deep yellow color which constrasted sharply to the dark brown oxidized appearance of specimens cut from molded billets. The yellow color indicated that little or no degradation from oxidation had occurred during cure and postcure and is no doubt related to the low porosity of the material. An interesting effect also connected to porosity is that the Hughes material would not sustain combustion in air whereas the Langley material, when ignited, will usually burn completely to a fine ash. Photomicrographs of fractured surfaces of Hughes and Langley material show a marked increase in homogeneity of the Hughes material (Figures 53 and 54). The large nylon particles, postcured microspheres, cracks and voids are no longer in evidence. Photomicrographs made at NASA Ames Laboratory show these features in greater detail. These photographs will be released in a forthcoming report from that facility.

3.5 SUMMARY OF THE DEVELOPMENT OF AN IMPROVED NYLON SYNTACTIC FOAM

The second phase of this investigation produced a reproducible analog (HFN Resin) of the commercial phenolic novolac and simple procedures for upgrading the nylon and microspheres. Specification for the raw material are found in Appendix VII.

A mathematical analysis of the volume fraction relationship of ingredients in the formulation provided a useful tool for changing the formulation. A molding process was developed which included the new features of dielectric preheating and molding to size. A comparison of the Langley and Hughes materials and processes is shown in Table 60.

The Hughes molding process was rapid, economical, and reproducible. Variation in density within molded nosecaps was not completely optimized but the process is amenable to refinement. The properties of the Hughes molded nosecaps are compared with the Langley Billet material in Table 61.
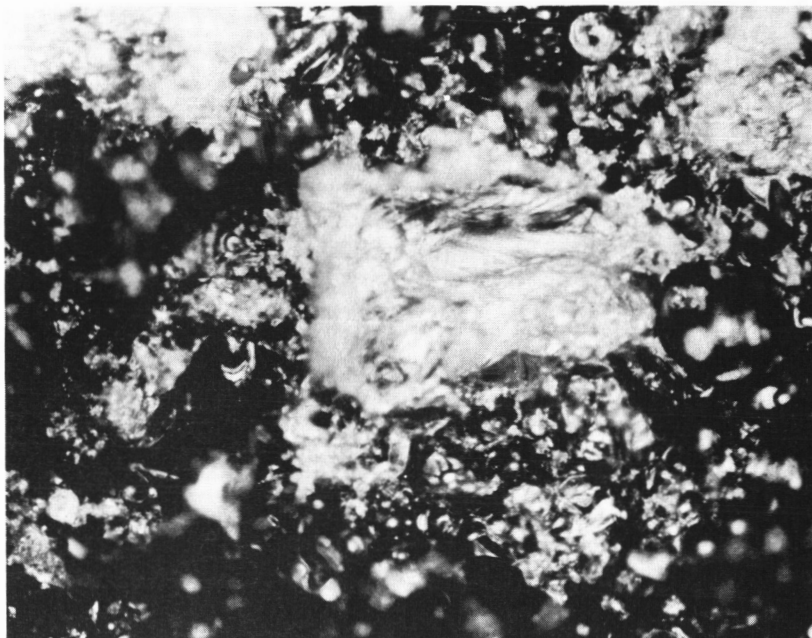
Figure 53. Photomicrograph (1000X) of fractured surface of Langley billet.
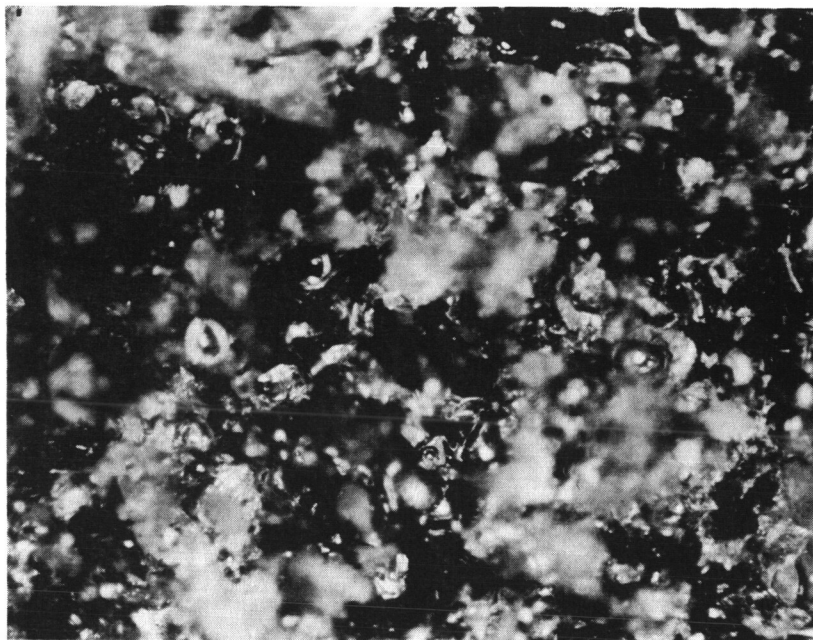
Figure 54. Photomicrograph (1000X) of fractured surface
of Hughes molded nosecap.

Item	Langley Billet Material	Hughes Molded Nosecap LAF #1 Formulation
Raw Materials		
Nylon	80 Mesh Average Powdered Nylon 66, 40 pbw	-120 Mesh Powdered Nylon 66, 40 pbw
Phenolic Novolac	Commercial grade, 25 pbw	Hughes HFN, 37 pbw

Table 60. Comparison of Langley and Hughes materials and processes.

Item	Langley Billet Material	Hughes Molded Nose Cap LAF #1 Formulation
Phenolic Micro-spheres	As received, 35 pbw	Sieved, (-50 mesh + 230 mesh), 23 pbw
Formulation		
Nylon	40% by weight	40% by weight
Phenolic Novolac	25% by weight	37% by weight
Phenolic Micro-spheres	35% by weight	23% by weight
Mixing Procedure	Low speed tumbling (Vee Blender)	Low speed tumbling (Barrel tumbler)
Molding		
Type of Mold	Positive Disk Mold 12" dia x 4" high Cylinder	Landed, Scout Nosecap Configuration
Pre-treatment	None	Shaped preforms dielectrically heated to approx. 200°F. (approx. 35 Sec.)
Molding Cycle	Material loaded in closed mold at room temperature, evacuated. Pressed to 1500-2000 psi. Pressure relaxed to 100 psi. Temp. raised from RT to 325°F (1/2 hr). Part cured in mold 20 hrs.	Shaped preforms loaded directly in hot mold. Press closed to lands at 150 tons. Pressure on material negligible. Cure cycle 90 mins. Molding ejected hot.
Postcure	Argon atmosphere 42 hrs to 300°F 21 hrs at 200°F, 4 hrs cool to 225°F	Argon atmosphere 12 hrs to 350°F, 6 hrs at 350°F. Cool to 100°F 6 hrs
Finishing	Machine all dimensions from billet	Machine approx. .100 from exterior surface only. (Can be molded to size)

Table 60 (continued). Comparison of Langley and Hughes materials and processes.

	Langley	Hughes
Density (dry) lbs/ft^3	33.0 - 34.5	34.0 - 36.0
% Volatiles (as received)	3 - 5%	3 - 4%
Total Porosity	50-55%	50-53%
Amount of Total Porosity Interconnected	60-80%	10-20%
Gas Transmission	+90 ml in 1 min.	15 ml max. in 1 min.
Compressive Strength	2000-3000 psi	3750-4550 psi
Tensile Strength	350 psi	1310 psi

Table 61. Comparative properties of Langley and Hughes molded ablator.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This work on the characterization and improvement of Nylon phenolic syntactic foam has shown that major improvements can be achieved by material and process optimization. The compressive strength, tensile strength and uniformity of micro-structures were significantly increased, and the porosity greatly reduced. It remains to be seen whether these improvements are accompanied by a significant increase in ablative efficiency. It is hoped that the improvements will add to the reliability of the material as a heat shield and also increase its ablative efficiency especially under high heat flux and high shear conditions.

The specific conclusions and accomplishments of this program are listed as follows:

Langley Billet Material and Process

1. The Langley billet molding process is well controlled and will probably produce uniform results if no changes occur in the raw materials.

2. The molded billets are uniform within narrow limits from billet to billet and within billets with respect to bulk properties.

3. The microstructure of the molded billets is heterogeneous.

4. The molded billet material is low in tensile and compressive strength and highly porous.

5. The raw materials used in the molded billet are variable from batch to batch. Other batches of the same material may cause great difficulty in producing a molded billet of similar properties.

Hughes Material and Processes

1. A reproducible analog of the commercial phenolic novolac was developed which can be produced with assurance of uniformity from batch to batch.

2. Simple procedures were developed for upgrading and increasing the uniformity of powdered nylon and phenolic microspheres.

3. A mathematical method was developed for optimizing the formulation of the three phase system consisting of nylon, microspheres, and novolac resin. This method proved efficacious in improving the formulation without modifying the density and nylon content. The technique should prove applicable to many other multiphase polymeric systems.

4. An efficient process was developed for molding of nylon phenolic syntactic foam into shaped parts. This process proved that dielectric preheating and direct compression molding of the syntactic foam are efficient and practical.

5. The properties of Hughes formulation (LAF #1) using upgraded raw materials and molded by the Hughes process were superior to those of molded billets. Tensile strength, compression strength, and uniformity of microstructure were greatly improved. Interconnected porosity and gas transmission were greatly reduced.

6. The Hughes molding process is amenable to strict process control and is suitable for scaling-up to large size. The fabrication of large heat shields by this method would be especially economical and attractive if jointed, overlapped or bonded assemblies could be used.

Recommendations

1. The Hughes molded material should be thoroughly evaluated under a variety of ablative conditions to determine whether the increased mechanical properties and homogeneity correlate with an increase in ablative efficiency.

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2. The use of the LAF #1 formulation and process for large heat shields should be investigated. First it should be determined whether close fitting joints and/or bonds in an ablating surface of this material cause more rapid erosion at the junction. If this is not so, then the possibility exists that large and reliable heat shields could be built up from many premolded segments. With such an arrangement very large heat shields could be made on existing equipment with a very low expenditure for tooling and labor. Furthermore, it has been shown by preliminary experiments at Hughes that the LAF #1 formulation can be molded directly onto phenolic fiberglass laminate and honeycomb substrates thereby producing a firmly attached structural base.

3. The mathematical relationships developed for the volume fraction relationships of the nylon-phenolic-microsphere composite may be used for the optimization of other multi-phase polymeric materials. It is recommended that the formulation of other ablative composites be optimized using this technique. The use of empirical approaches to attain optimum formulation would thereby be eliminated and a considerable reduction in development time and cost would result.

5.0 ACKNOWLEDGEMENTS

In order to accomplish this intensive effort during the short time available many persons contributed their efforts and talents. Dr. John Parker of the NASA Ames Laboratory supported and encouraged this work with enthusiasm and unusual technical insight. Mr. William Brooks of the NASA Langley Laboratory and his associates were most cooperative and helpful.

At Hughes Aircraft Company special recognition should be given to Mr. David Horwitz for controlling and recording the myriad of details and test results, to Mr. B. G. Kimmel for sound chemical characterization and formulation; to Mr. Charles Bahun for mathematical and statistical analysis, and to Dr. Stewart Eglin and members of his group for polymer synthesis.

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APPENDIX I

NON STANDARD TEST METHODS

FREE AND COMBINED AMMONIA

Small samples (approximately 5 gm) were cut from an eight-inch diameter by two-inch thick cylindrical billet from NASA-Ames. Samples one half inch thick were cut from the center of the billet.

The sample was ground and boiled in dilute sulfuric acid. After filtering, excess caustic was added to the filtrate. A faint smell of ammonia was detected for both types of sample.

The process was repeated, except that the liberated ammonia was trapped in a known excess of standard acid. Back-titration yielded an ammonia content of 0.166% for the top sample and 0.178% for the center sample.

DENSITY AND COMPRESSIVE STRENGTH

Compressive strengths and density (per ASTM-D-695) were calculated from specimens 0.505 inch diameter by one inch high and 1/2" x 1/2" x 1/2" cubes respectively. The specimens were cut from the Ames billet at randomly selected locations. Specimens cut from the Langley billet section were selected with an orientation for both radial and altitude but not circumferential location. The circumferential location could not be determined at this time. The altitude location may be inverted since no top or bottom orientation was indicated. The preliminary compression and density testing clearly indicates differences dependent upon relative location within the billet.

EXTRACTION OF HEXAMETHYLENETETRAMINE

Using the Hobart mixer and 20 gallons capacity kettle, weigh 5 pounds of powdered resin and add 10 gallons of distilled water.

A-1

Start mixer in position number 3, maintain it running for 2 hours and filter resin. Filter through large Gooch filter and dry overnight at room temperature.

Repeat procedure six times or more until gel time is in excess of 50 minutes. Typical gel time results are as follows:

Gel Time Minutes	8	23.20	28.20	31.10	32.15	55.24
No. of Washes	1	2	3	4	5	6

STANDARD TEST METHODS

Impregnation of ablator material with epoxide resin and determination of continuous porosity content.

A. Specimens

Small precisely machined specimens of known dimensions and volume. The standard Hughes specimen was a half inch cube or a 0.750 inch dia x 1 inch high cylinder. All dimensions measured to ± 0.0005. Other shapes and sizes of specimens may be used provided the volume is of the same magnitude.

B. Materials

Epon 828 Epoxide Resin (Shell) 22L-0803 Amine hardener (Bakelite)

C. Equipment

Micrometers

Analytical Balance

Vacuum Desiccators equipped with addition funnel and stopcock

Pressure chamber, 50 psi, dry nitrogen

D. Procedure

1. Dry specimens under vacuum at 120°F for 8 hours. Weigh to nearest 0.0001 gm and measure ± 0.0005 inch. Store in desiccator.

2. Place specimens in beaker in vacuum desiccator. Evacuate air to 28 inches of water vacuum.

3. Mix resin and hardener in proportion 100 pbw Epon 828 to 37.5 pbw 22L0803.

4. Add sufficient resin to beaker then funnel to completely immerse specimens, do not break vacuum. Continue until no bubbles are seen on surface of resin.

5. Transfer beaker to pressure pot chamber, inject 50 psi of dry nitrogen. Maintain pressure for 1 hour.

6. Remove specimens, clean and wipe with a damp rag with acetone. Weigh to nearest 0.0001 gm and record resin pickup.

7. Cure in oven at 120°F for 6 hours, cool to room temperature.

8. Weigh to nearest 0.0001 gm, recheck dimension, calculate density.

E. Sample Data Sheet and Calculations

Heading	Value (Example)	Calculation
Sample Number	A3-D2-R3	
Dimensions - inches	0.748 dia x 0.500	
1. Volume - inches^3	0.2197	
2. Volume cm^3	3.6009	
3. Initial weight - gms	2.0391	
4. Initial density - gm/cc	0.566	$D = (3)/(2)$
5. Impregnated, uncured wt-gm	3.4620	
6. Density, impregnated, uncured - gm/cc	0.961	$(5)/(2)$
7. Weight of resin uncured - gm	1.4229	$(5)-(3)$
8. Volume of uncured resin - cc	1.305	$\dfrac{(7)}{1.09}$
9. Cured weight - gm	3.4432	
10. Density of cured specimens gm/cc	0.956	$\dfrac{(9)}{(2)}$
11. Weight of resin cured - gm	1.4041	$(9)-(3)$
12. Volume of cured resin - cc	1.190	$\dfrac{(11)}{1.18}$
13. Actual density of microspheres in composite - gms/cc	0.287	$D_M = \dfrac{(10)}{2.857-1.565 \times (10)}$

E. Sample Data Sheet and Calculations (Continued)

Heading	Value (Example)	Calculation
14. Volume of solids in composite - cc	1.685	$\frac{(3)}{1.21}$
15. Total volume of voids - cc	1.916	$(2)-(14)$
16. Discrete voids as % of total vol.	17.0	$\frac{(15)-(18)}{(2)} \times 100$
17. Impregnated voids as % of total vol.	35.2	$\frac{(8)}{(2)} \times 100$
18. Impregnated (continuous) voids as % of total void volume	68.1	$\frac{(17)}{(17)+(16)} \times 100$

SPIRAL FLOW TEST - COMMERCIAL PHENOLIC NOVOLAC

Tooling: Mesa spiral flow mold with 2" diameter transfer pot and plunger

Equipment: Erie ASTM flow press with calibrated pressure gauge, 1 KW Mytron dielectric preheater

Molding Conditions: Temperature - as specified $\pm 5^{\circ}$F

Press Load - as specified using standard press settings

Closing speed - full capacity

Charge weight - 35 gm

Results:

Record a) Length of well molded flow-inches

b) Total length of flow-inches

c) Closing time

d) Temperature, time closing, press load

e) Appearance of molding

f) Pre-molding treatment

MOLECULAR WEIGHT DETERMINATIONS OF HFN-1, LFN-3, AND COMMERCIAL NOVOLAC

Discussion

All determinations were made ebulliometrically, using standard Cottrell-Washburn[*] ebulliometers especially equipped with loading tubes having standard taper orifices (blown onto the ebulliometers

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[*]See Figure A-1

directly below the condensers). The boiling point elevations were obtained using Beckman differential thermometers read to a precision of ±0.005 centigrade degrees.

By the use of the method of comparative measurements, the necessity for taking barometric variations into consideration was eliminated. Further, a number of refinements of the method were thought unnecessary[*] in view of the level of accuracy required: refinements such as mandstatic control of the entire system, comparative thermometer calibration, determination of dead-space, high fractionation of ebulliometric solvent (dioxane), etc.

Determinations of concentration were obtained gravimetrically by removal of samples directly from the elevation ebulliometer in the usual manner in all cases, simultaneous controls were run on the concentration determinations, and the error factor (usually ≈ 1% by wt) was entered into the calculations.

It was found, during standardization of the solvent, that at least 10 hrs. were required, between successive concentrations, for equilibrium of the system to be maintained. (This was in agreement with previous experience using other solvents).

Calculations were made on the basis of the averages of 20 readings per concentration; and from these averages, a regression curve was obtained. The molecular weight at zero concentration was in each case the point reported here.

Experimental

Two identical, well insulated ebulliometers were loaded with 150 ml each of dry, reagent grade dioxane (all determinations were made using dioxane from a single bottle, and the K_B for this bottle of dioxane was determined using a dried reagent grade p-terphenyl as

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. [*]Surface activation of the ebulliometers was not done, since experience showed that scratching the inside surface of the percolator bell, together with the use of capillary tubes, assures satisfactory evenness of boiling and solvent delivery to the thermometer bulb.

PRESSURIZING BULB
(FOR CONC. SAMPLES)

WEIGHING TUBE AND BLOWN-IN
LOADING TUBE

DIFFERENTIAL THERMOMETER

SOLVENT DELIVERY JETS

CONDENSER

GLASS WOOL-
ALUMINUM FOIL
INSULATION JACKET

THERMOMETER BULB

SOLUTION LEVEL

EXTRACTION TUBE
(FOR CONC. SAMPLES)

GLAS-COL CYLINDRICAL
HEATING MANTLE

PERCOLATOR BELL
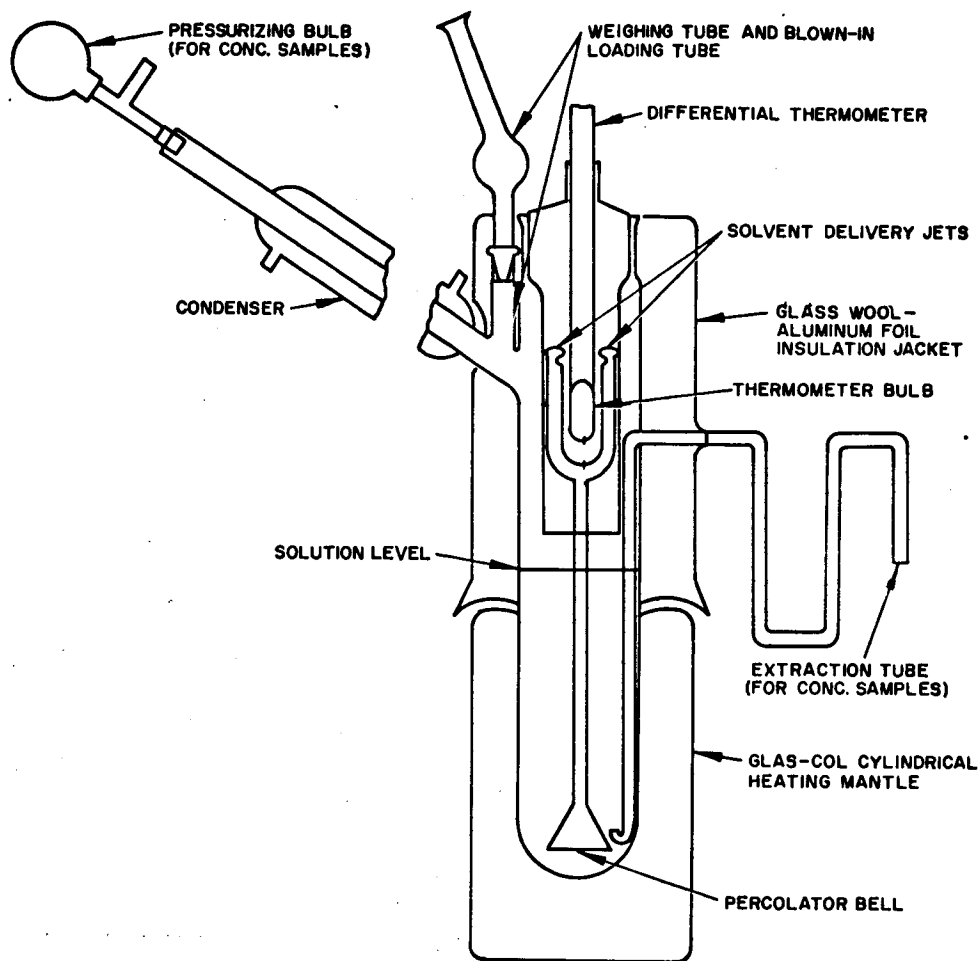
Figure A-1. Sketch of Molecular Weight Apparatus (Ebulliometer).

standard solute).   The pure solvent was boiled 3 to 5 hours before
obtaining the thermometer differential for the zeroth concentration.

Addition of solutes was made in solid form rather than in solution.
The loading was done by diverting the vapors from the condenser through
an especially constructed weighing tube which had two orifices blown
into it.   In this way, the solid solute could be washed into the ebullio-
meter by fresh hot solvent condensing on the weighing tube.

Four successively larger concentrations were used in all three cases, allowing 10 hrs. to lapse between loading and the taking of elevation readings. 20 readings were taken for each concentration, the readings being taken 2 minutes apart. (This included the zeroth concentrations as well.) In obtaining samples for the determination of concentration, the ebulliometer was pressurized with an ordinary pipette bulb fitted with a connection to the upper end of the condenser. In this way, the extraction tube of the ebulliometer could be flushed out, and the samples, withdrawn with minimum disturbance of the system. A total of approximately 5 ml of solution were extracted in each case, (including preflushing of the extraction tube). The concentration samples, being soluble in cold solvent, were weighed by difference into small flat pans, and the solvent was pre-evaporated from the pan to near dryness, leaving a thin film of the solute. The residue was then washed several times with acetone, and final evaporation performed in a vacuum oven at approximately $50^{\circ}C.$, 20-30 mm Hg. In each gravimetric determination, a control was run simultaneously with the concentration, and a correction factor was applied to the determination based on percent by weight solvent.residue. The residue error amounted to $\leq 1 \%$ by weight.

Calculation of Molecular Weight

The average zeroth delta was obtained in each determination and molecular wt points calculated at each concentration as follows:

$$MW_n = \frac{K_B \times C_n}{(\overline{\Delta}_o - \Delta_n)}$$, where: MW_n = Mol. Wt. at n'th concentration

C_n = Concentration in gm solute per Kgm solvent

$\overline{\Delta}_o$ = Average zeroth delta.

$\overline{\Delta}_n$ = Delta at n'th conc.

K_B = Ebulliometric constant

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*Deltas were obtained by difference between pure solvent reference reading, and elevation reading.

A-7

Calculation of Regression Curve

In each case, the average molecular weights for the various concentrations were used as abcissa in the regression curves. The least squares curves were obtained from the following simultaneous linear equations:

$$\sum \overline{MW}_n = n\,a + \sum C_n\,b$$

$$\sum \overline{MW}_n \times C_n = \sum C_n a + \sum (C_n)^2\,b$$

where

$\overline{MW}_n$ = average Mol. Wt.

n = No. of concentrations

C_n = Concentrations

and the regression equation:

$$\widehat{MW} = a + C\,b,$$

where

$a = \overline{MW}$ at zero concentrations

(See Figures A-2 thru A-5.)
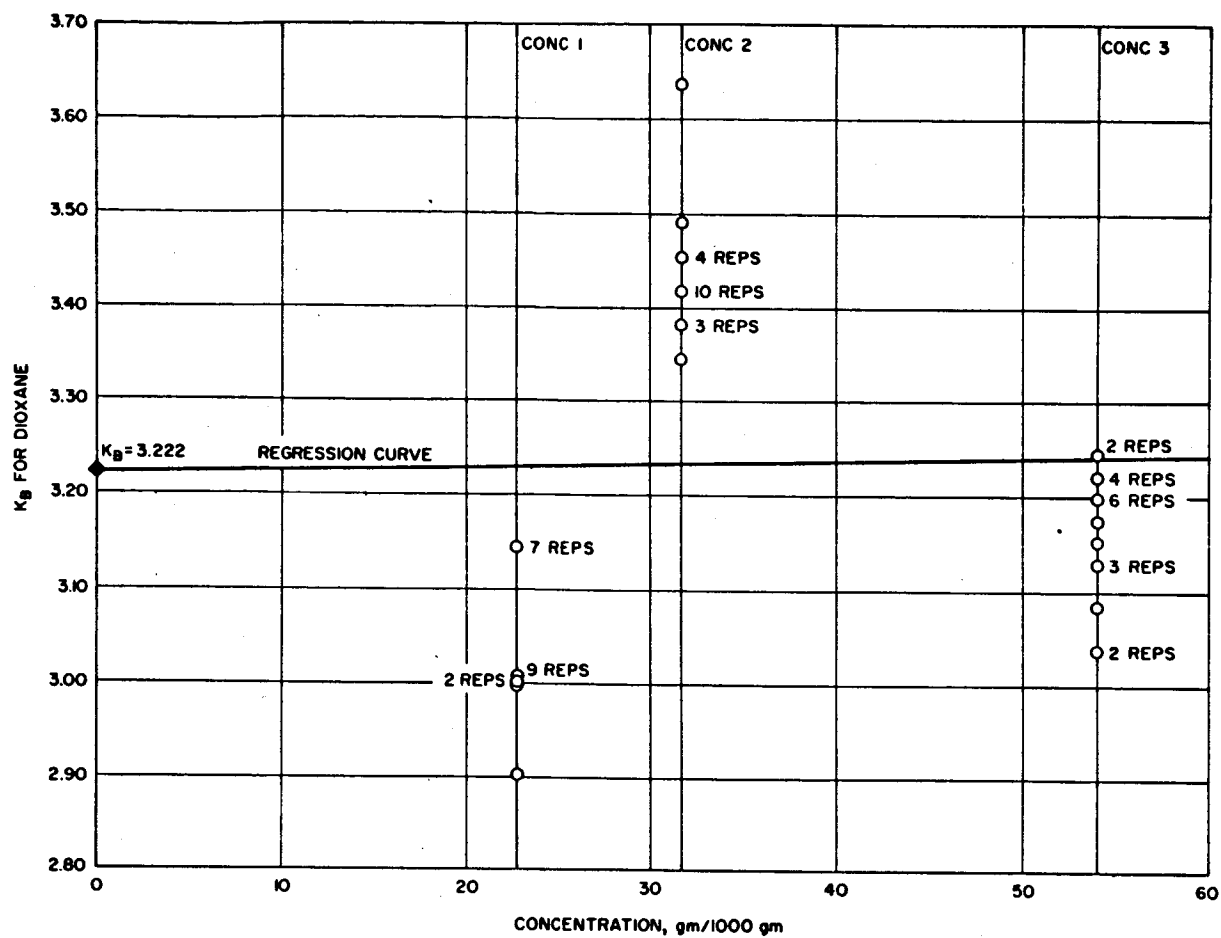
Figure A-2. Molecular Weight Determination for HFN-1.
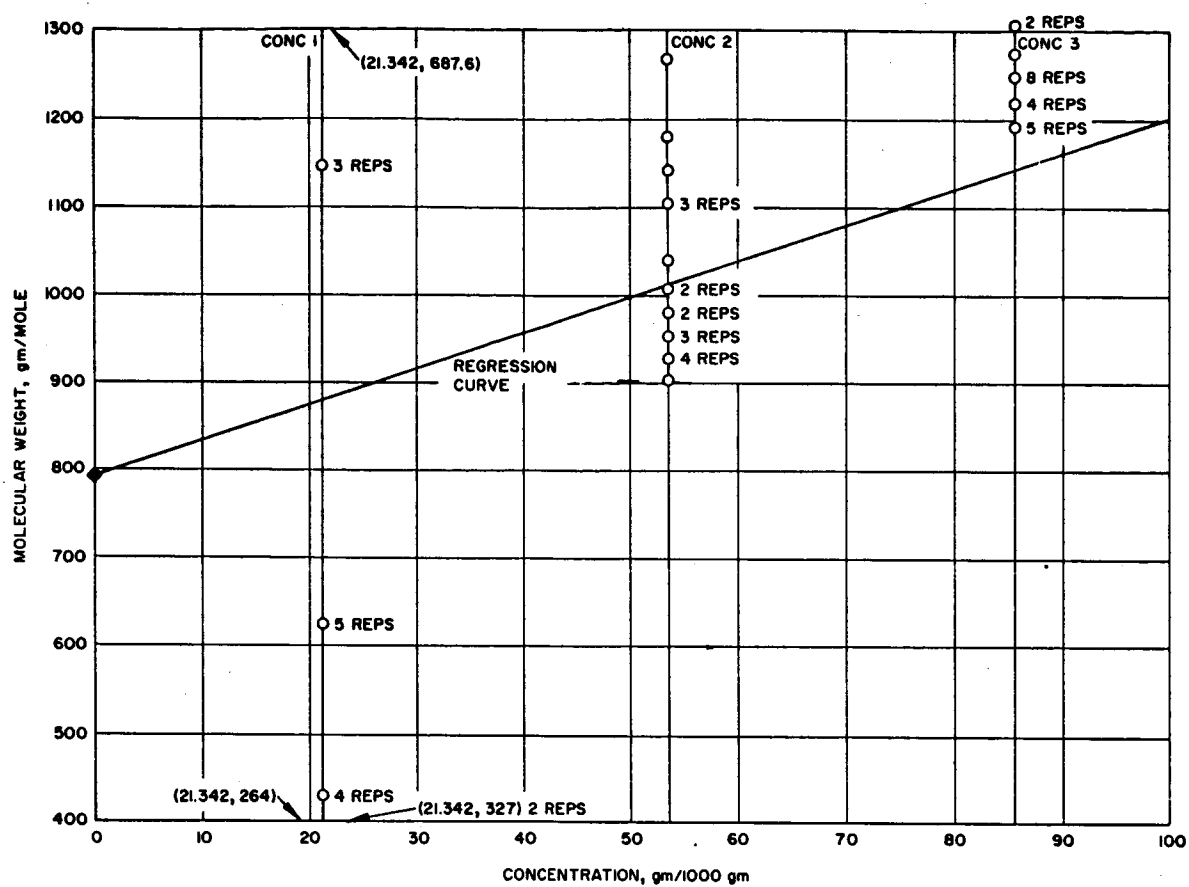
Figure A-3. Molecular Weight Determination for LFN-3.
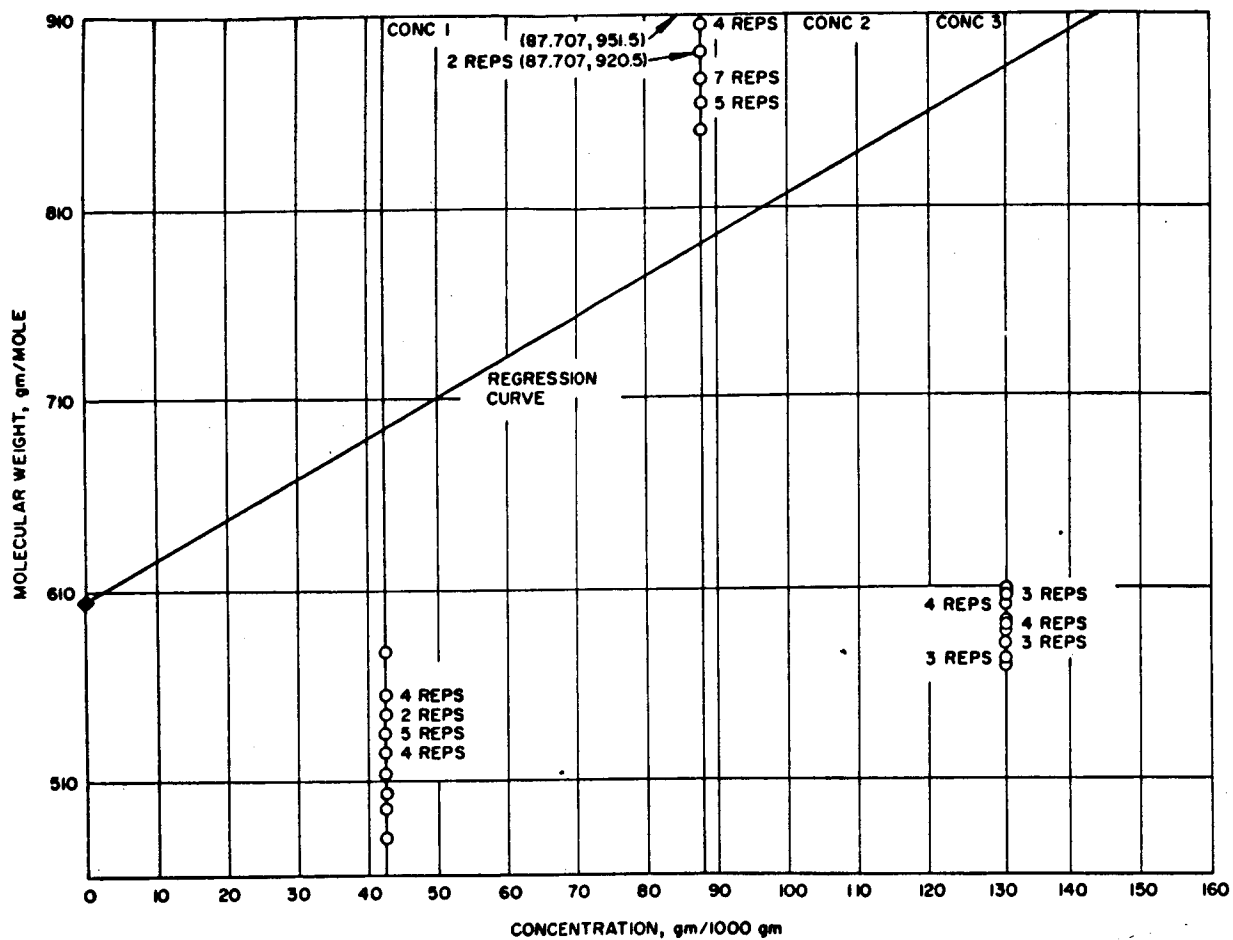
Figure A-4. Molecular Weight Determination
for Commercial Novolac.
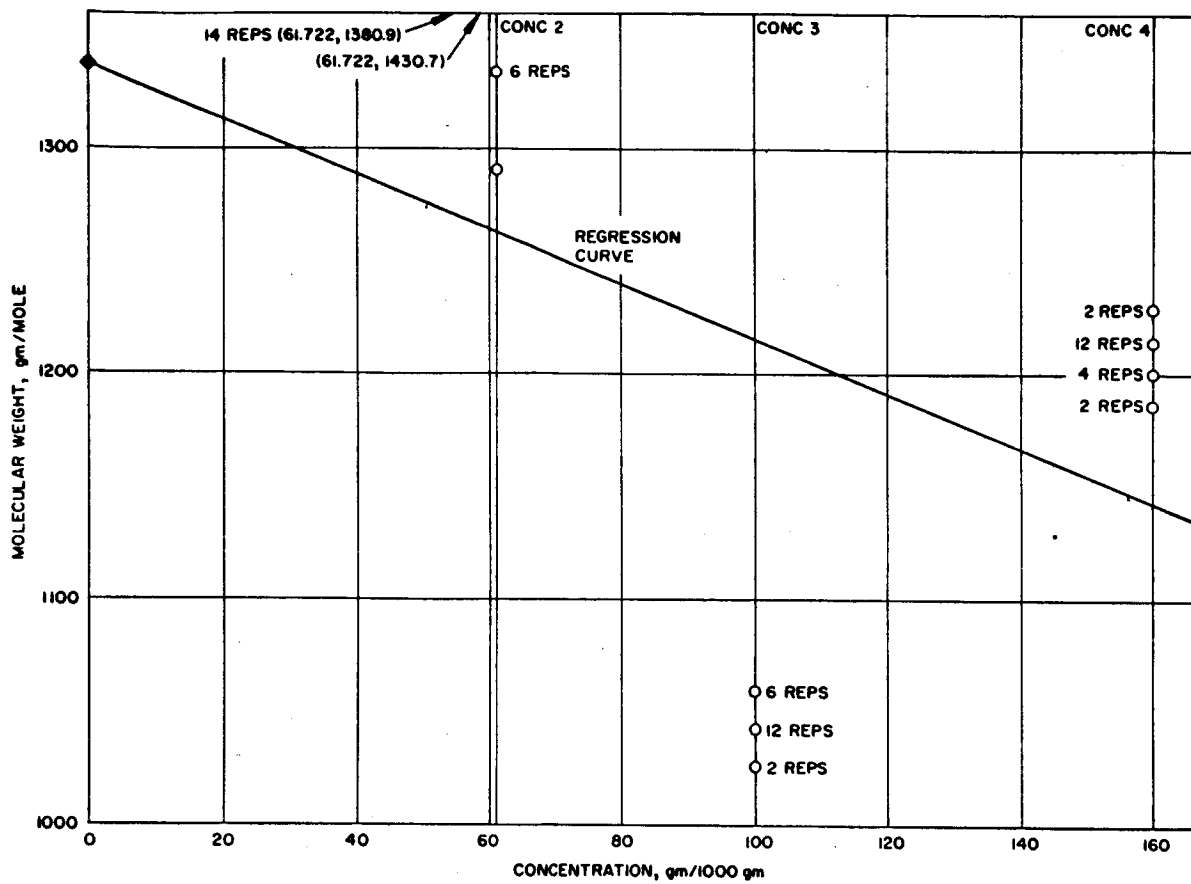
Figure A-5. K_B for Dioxane

PROBABLE SOURCES OF VARIABILITY IN COMMERCIAL RAW MATERIALS

RESIN

The following factors are major sources of variability in the manufacture of pulverized Novolac Resin.

Resin Synthesis

Raw materials

Phenol or tar acids
Formaldehyde
Acid
Hexamethylenetetromine

Equipment (resin making)

Weigh tanks
Kettle size
Kettle material
Kettle condenser
Discharge and storage pans

Operating conditions

Cooling water
Storage

Pulverizing

Batch blending
Equipment

Packing

RAW MATERIALS

Phenol

Because of its orthocresol content, phenol from coal tar distillate is not interchangeable with synthetic phenol. Actually synthetic CP phenol is obtainable at a premium of only 2-3¢/lb and hence there is little economic advantage to be gained by the substitution.

There is more risk of contamination with tank car delivered product than with the drum product. However, a color and melting point standard should be sufficient for the quality control of synthetic phenol.

Formaldehyde

In the synthesis of phenolic resins this compound is usually used as the 37% solution (formalin), available in two versions.

The so-called inhibited version contains methanol and is insensitive to aging. However, it reacts more slowly with phenol than the alcohol-free material and there is reason to believe that some methoxy formation occurs.

The methanol-free solution tends to change on aging. The formaldehyde polymerizes so that in time a heavy flocculent precipitate of paraform settles out. In addition, the Cannizarro reaction results in the formation of formic acid.

The loss in yield due to the acid formation is of far less importance than the resulting change in pH. Unless this change is compensated for by a reduction in catalyst, the reaction rate will be affected.

Acid

The acid catalyst is not likely to be variable per se. That is, any variability will probably be the result of human error in handling after opening the container. In the usual oxalic-acid-catalyzed reactions the acid is added in portions until the pH is within the specified range before heating the mixture.

Hexamethylenetetramine

This product can vary due to moisture content. This variability can come from two sources: (1) failure to remove water in centrifuging the crystals and (2) exposure to humid air while store in open bins.

In addition, the amount per pound of resin is deliberately varied to obtain a controlled gel time (i.e., to compensate for variable resin).

RESIN MAKING EQUIPMENT

Weigh Tanks

Unless the weigh tanks are allowed to drain thoroughly between raw material charges the ratios of the starting ingredients will vary and therefore the molecular weight of the finished Novolak will vary.

In addition, if the weigh tanks are used for a variety of products, small amounts of ingredients not called for by the recipe can get into the product.

The above remarks also apply to the piping. Here the problem will be more serious for kettles far from the weigh tank than for the nearer kettles.

Obviously all of this variability can easily be eliminated by precisely specifying procedures.

Kettle Size

This can have an effect because of differences in heat transfer rates. However, its main effect seems to be on the resin color. Whether this metal contamination has an adverse effect upon the high temperature stability of the resin is a moot point. On the other hand it is hardly likely to have a beneficial effect.

In any case for production of light-colored resins glass-lined or stainless steel kettles are preferable to cast iron, nickel and copper.

Condenser

Condenser tubes can become coated with paraform or entrained resin during the dehydration cycle. In the violently exothermic portion of the reflux cycle of the following batch flakes of the coating can get dislodged and carried into the resin.

Another source of contamination is the kettle wall itself where material can get baked on during the dehydration cycle.

Actually both kettle and condenser should be thoroughly cleaned after every batch even if only one product is being run in a series of batches.

Discharge-Storage Pans

Usually novolaks are discharged into steel pans stacked so that cascading can take place, thus eliminating the necessity of shuffling the pans of a given stack with a fork lift truck. Thus there is a degree of mixing in this operation.

However, during the discharge cycle liquids (water, phenol, etc.) are draining from the line to the condenser and also refluxing from the kettle head and are accumulating on the resin surface. This accounts for the difference between the last fraction of the discharge and the first.

Since the pans are uncovered while in storage dust, dirt and even foreign resin can accumulate on the resin surface.

In removing the solid cold resin by hammering lumps of resin can be left adhering to portions of the pan (e.g., corners) to contaminate a subsequent resin.

Simple awareness of these sources of variability should be sufficient to lead to their elimination.

However, if high purity material is to be made in glass-lined equipment then it is taking an unnecessary risk of metal contamination to discharge into steel pans. Therefore use of Teflon-coated pans should be considered.

Variability of some resin properties can be expected to have a pronounced effect upon the molded billet properties. In molding the material the resin melts, flows, and gradually increases in viscosity until gelation occurs. It is evident that these phenomena are dependent upon particle size and distribution of the resin melting point, viscosity, and curing rate (or gel time) and that these properties must be controlled.

For example if particle size is too large, melting point too high, viscosity too high, and gel time too short, curing will occur before sufficient flow has taken place. Thus filler particle will not be wet with resin and weak bonding will occur. Obviously control of only one of these properties is insufficient to insure density and strength control in the finished billet.

Considerations such as the above will show that because of the low thermal conductivity of the material, "case-hardening" should occur, resulting in a porosity gradient in the billet. It is evident that the degree of this variability will be highly affected by the resin properties.

NYLON

The following properties are considered to be the most likely sources of variability in the nylon.

- Moisture content
- Amount and type of inorganic constituents
- Molecular weight distribution
- Particle distribution
- Contamination

The moisture content of nylon can run as high as 2.5 percent under ordinary conditions of humidity and temperature and as high as .8.5 percent under extreme conditions. Large amounts of moisture in the nylon can cause error in compounding a molding material. In addition, the resulting molding material may have undesirable molding properties or yield parts with undesirable physical properties.

The amount and type of inorganic substances can influence the properties of the nylon, particularly if such substances have been added to enhance the high temperature properties.

Large variations in the molecular weight distribution will affect the melting point range and possibly the ablative properties. It is not believed that a high-production polymer of this type will exhibit significantly large variations in molecular weight.

The particle size distribution of the nylon can have a pronounced effect on the ablative properties of the molded composite containing it.

Large amounts of contaminants will undoubtedly influence the ablative properties. The observance of ordinary precautions in the formulation of molding material and the fabrication of billets should make this potential source of variability insignificant.

PHENOLIC MICROSPHERES

It can be assumed that the phenolic resin used in the manufacture of microspheres will be more uniform than the commercial novolac. This assumption is made on the supposition that resin for microspheres must be controlled in melt viscosity, curing time, surface tension, and

other properties in order to assure high production and economy in the subsequent blowing operation. However, the sources of variability discussed for novolac resin will also apply to the raw resin for microspheres but to a lesser degree.

The blowing process for the production of microspheres is also a source of variability. The diameter, shape, wall thickness, and distribution of these factors are known to be variable. Impurities may be introduced by the blowing agent and from the reaction and handling equipment. Finally, the degree of damage to the microspheres due to handling, transportation, and storage is another source of variability in the final material as used by the formulator.

APPENDIX III

SAMPLING AND TESTING PLAN FOR LANGLEY ABLATOR
BILLETS AND RAW MATERIALS

1. Introduction

This is the detailed test plan for the Ablation Materials Study Program (NAS 2-2739). The plan includes a list of the tentative tests for each category of material, the number of tests planned, the statistical approach and level of confidence for each of the investigations. Also included is a program schedule for the various phases of the investigation.

2. Summary

The evaluation of the billet variability will be done in several steps.

2.1 The whole billet will be checked for overall appearance by visual and X-ray examination, and for density.

2.2 The billets will be thoroughly sampled and tested throughout according to a detailed statistical plan using rapid and economical tests such as density, compressive strength, moisture content, etc. The results will be analyzed statistically.

2.3 Selected areas, and areas showing significant variability in step (2) will be subjected to more complex tests including, porosity, microscopic examination, T.G.A., degree of cure, IR spectroscopy, ash content and spectral emission, and ablation tests by Ames Laboratory.

An additional check on the variability of the Langley material will be provided by testing of the formulation samples for each billet.

The raw materials for each billet will also be sampled and tested to determine whether raw material variation correlates with molded billet variation.

3. Sampling and Testing of Molded Billets

3.1 The total volume of each billet will be divided (conceptually) into equal sub-volumes from each of which a constant fraction, symmetrically located within the sub-volume, should be drawn.

Data obtained on samples drawn in this way can be used to calculate the mean value of any given property without weighting the individual readings. That is, we use

$$x = \frac{\Sigma x}{N}$$

rather than

$$\overline{x} = \frac{\Sigma f_i x}{\Sigma f_i} .$$

The first two billets will be intensively studied to determine whether each property is constant throughout the volume of a billet and if not whether its contours are symmetrical or not. Therefore, the sampling volumes have been selected so that complete symmetry is maintained. Otherwise it will be impossible to determine whether asymmetry is actually present or whether it simply reflects an inadequate sampling plan.

By complete symmetry is meant symmetry with respect to the billet axis and to a plane through the center of gravity and normal to the axis.

On each of three equal discs cut from a billet, samples will be drawn along 120° lines and within circles as illustrated in Figure A-6.

3.2 Analysis of Variance

An analysis of variance will be used to study the data.

It might be well to consider some of the possible results of the analysis of variance of some property such as cure. This property could be affected by non-uniform heating and the analysis could be interpreted from this stand point.
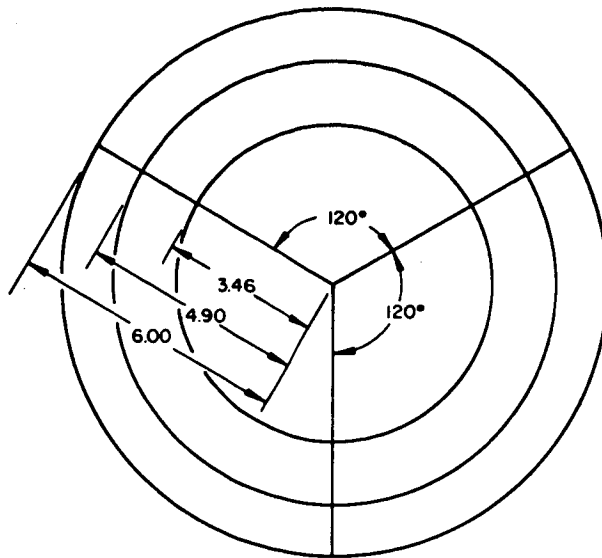
Figure A-6. Three Nesting Cylinders of Equal Volume

Assume a complete factorial experiment using as factors the specimen coordinates (axial height, angular distance from index mark on circumference, and radial distance from axis). The analysis will yield the effects of these three primary factors plus the four interactions. Let us consider some simple idealized cases.

Case 1. None of the factors are significant. The material is homogeneous throughout its volume. Samples can be drawn at random and differences will represent error only.

Case 2. Axial height significant. This is equivalent to stacking discs differing in cure to form a billet. Could arise in idealized heating of a cylinder if one flat face is a heat source and radius is infinite in length, for example.

Case 3. Circumferential factor significant. This is equivalent to stacking wedges differing in cure around the axis to form a billet. A surface source heating model which would give only this cure pattern cannot be constructed.

Case 4. Radial factor significant. Equivalent to nesting hollow cylinders differing in cure. Heat source is curved surface and axis is indefinite.

Case 5. Significant interaction of axial and radial factors. Equivalent to stacking discs some of which show a radial effect while others do not. If all of the mold surfaces were maintained at constant temperature then due to mold geometry heat paths would be quite different in length. This would give rise to this case.

Case 6. Significant interaction of axial and circumferential factors. Equivalent to stacking discs made of different wedges. Again a surface source heating model could not give this result.

Case 7. Significant interaction of circumferential and radial factors. A line heat source parallel to the infinite axis and on the curved surface could give this result.

Case 8. Significant interaction of all three factors. One or more point heat sources at the mold walls could give this result.

Thus if there is a significant variability within billets due to heat transfer then it is likely to involve the axial and radial factors rather than circumferential. This would indicate that an experiment should include more levels of the former than the latter. However, due to the possible complications of interactions it would be advisable at present to keep the number of levels of each factor at three.

The significance level for all statistical tests will be .01.

3.3 Sampling Procedures

3.3.1 Langley Billets

The sampling plan is based on the selection of 6 billets chosen at random from a set of 10. The 30 billets have been grouped by fives in the order of molding and one billet selected at random from each group. By this procedure it will be possible to subtract a trend (or "learning") variability from the apparent billet variability to estimate a true billet variability. The random selection is 2, 8, 12, 19, 22, and 26.

A very exhaustive evaluation of one or more billets by all significant tests listed is necessary for the following reasons.

(1) To determine whether there is a significant variability within billets.

(2) To determine whether the variability is such that it can be eliminated in a subsequent step (say increased postcure). Thus under-cure would be remediable while porosity would not.

(3) To determine the precautions to be taken in sampling billets.

(4) To estimate the possibility of eliminating the variability by changes in molding.

    (a) Molding to shape

    (b) Electronic pre-heat

(5) To determine whether any tests can be discarded.

Before discussing the sampling to be used it might be well to consider how variability within billets could arise. Due to assymetries in construction there are always present to some extent relative heat sinks and sources in the mold itself and hence there is non-uniform heating of the molding material. In addition, due to the nature of the material there are likely to be steep pressure gradients even if heating is uniform. Thus there will be marked differences in flow from point to point.

The above could result in

(1) Uneven curing throughout the mass.

(2) Non-uniform porosity.

(3) Filler particle segregation by size into flow planes.

Such a material would probably be variable from point to point with respect to most properties but not in a random manner. That is, the isopleths of a property will be continuous surfaces within the billet. To detect this type of variability sampling will have to be done geometrically with respect to a constant orientation in the mold.

Sampling will be carried out by taking surfaces normal to the axial, radial and circumferential directions. If taken by threes as indicated in Figure A-7 there will be a total of 27 locations from each billet. For each test two adjacent specimens will be cut from each of the 27 locations. Each specimen will be labelled as to location in the billet and assigned at random to one of two piles (testing replicates). The 27 specimens of a replicate will be tested in random order. The data will be recorded on forms having testing order and specimens identification specified in advance. A sample sheet is shown at the end of this section.
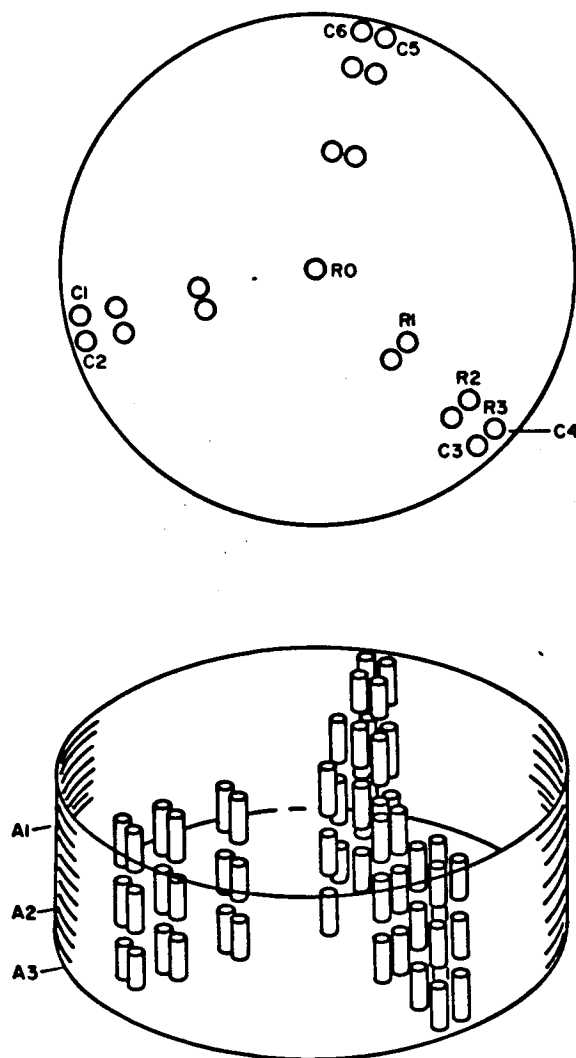

Figure A-7. Compression Specimens Locations and Identification.

As soon as the data of both replicates of a given test have been obtained, an analysis of variance will be performed to determine the nature of the variability. However, regardless of the results of this analysis another billet will be evaluated exactly like the first billet. The reason for repeating the series of tests with another billet is to obtain the information necessary to distinguish between biases and random billet variability. That is, to distinguish differences between points to all billets from those peculiar to the first billet (due possibly to the particular batch of material and its molding or processing conditions).

The knowledge gained from the analysis will be applied immediately to the sampling of the remaining billets. If no bias is found, specimens will be taken at points randomly selected from billet to billet. In the contrary case, sampling will be done within the same specified volume of each billet. If more than one volume is sampled each specimen of a billet must be identified by volume location.

Aside from the reduced sampling and possible reduction in the number of properties measured, the procedure for evaluating the remaining billets will be the same as for the first two. Analyses of these data will reveal whether there are significant billet differences for the properties tested.

3.3.2 Langley Formulation Samples

Samples of the mix used to form billets at Langley will be subjected to testing in the following manner. Approximately 100 grams will be used to mold a billet model at one fourth scale. This molded model will be used to fabricate compression specimens. The cured properties will be evaluated from the model.

The properties of each model will be correlated to the full size billet. Properties of those billets which are not shipped to Hughes Aircraft will be predicted from the models. The modeling provides a technique for evaluation of the synthesized molding mixes. The model evaluation will be used to predict the properties of full scale billets and/or nose cones.

Two randomly selected samples of each billet mix and raw material will be tested for each response. A single factor analysis of variance will be performed to determine whether there is a significant difference between mixes. In addition, quality control charts ($\overline{X}$ and R) will be prepared for possible use in the future. The sampling instructions for the raw materials of each Langley billet mix are shown in Appendix A.

3.4 Weighting and Ordering of Tests

The weighting and ordering of the tests performed in this program are vitally important to the final outcome. Testing will be broken down into five categories:

(1) Billet Tests

(2) Moldable material tests (Langley formulation mixes)

(3) Phenolic Microballoon tests

(4) Phenolic resin tests

(5) Nylon tests

Two groupings will be employed; destructive and non-destructive investigation. In general, the tests will be ordered to enable the completion of non-destructive tests on samples which may later be used in a destructive test. For example, the moisture content sample may be also used for compressive strength testing. Tests such as these can be performed with the same sample and actually save effort since the compressive specimen should be brought to standard conditions of temperature and moisture content before testing. The destructive tests will all require separate specimens, therefore their ordering is not required.

The weighting of tests will also be extremely important, however, at this time there is very little that can be said about the relative importance of the various tests. It is difficult to assess the value of controlling material properties until each of the variances have been correlated with ablation properties. The tests under consideration at this time are listed in the following table.

A. Billet Tests
 X-Ray Examination
 Compressive Strength
 Moisture Content
 Extractables
 Extent of Cure
 Bulk and Apparent Density
 Ash Content
 Average Size and Count of Component Aggregates
 Porosity
 TGA
 IR Emission
 Ablation Testing (Ames Labs)
B. Moldable Material Tests
 Material Mixture Sampling
 Particle Size and Distribution
 TGA
 Infrared Analysis
 Resin Content
 Flow and Viscosity Index
C. Phenolic Microballoon Tests (Raw Material)
 Weight Fraction Damaged
 Apparent Density
 Particle Size and Distribution
 Particle Density
 Effect of Pressure on Flotation
 TGA
 Infrared Analysis
 Nitrogen Analysis
 Moisture Content
 Ash Content
 IR Emission
D. Phenolic Resin Tests (Raw Material)
 Wet Analysis
 Infrared Content
 Emission Spectra
 Moisture Content
 Viscosity
 Viscosity Index
 Molecular Weight Distribution
 Particle Size and Distribution
 Gel Time
 Melting Point Flow
E. Nylon Tests (Raw Material)
 Infrared Analysis
 Nitrogen Content
 Ash Content
 Moisture Content
 Molecular Weight
 Melting Point
 Particle Size and Distribution
 TGA

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3.5 Testing Program

The five categories of tests will each have a group of tests selected for the particular material. Not all the tests listed will be performed on all samples because of (1) the limited amount of material available and (2) some tests may not be sufficiently precise to show variability. The test categories and their respective tests are as follows:

3.6 Code for Specimen Identification

Specimen will be coded for each material to enable simple identification.

First Position Billet No. or Mat'l	Second Position Type of Test		Third Position — Location of Billet		
			Altitude from Base	Radical Position	Circumferential Angle
2	TGA		A_1	R_1	C_1
4	IT		A_2	R_2	C_2
9	COM	- Compression	A_3	R_3	
10	PSD	- Particle size and distribution			
15	MC	- Moisture content			
17	XR	- X-Ray			
19	AC	- Ash content			
23	NC	- Nitrogen content			
	MP	- Melting point			
	MW	- Molecular weight			
	VIS	- Viscosity			
	WET	- Wet analysis			
	GEL	- Gel time			
	FLO	- Melting point flow			

Prefixes: A - Ames; L - Langley; X - Experimental; R - Resin;
N - Nylons; B - Microballoons

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Addendum A - Sampling Instructions for Langley Billet Formulation

The sampling instructions for Raw materials used in ablative formulation are as follows:

1. Take approximately 25 percent by weight more than needed for each batch of formulation.

2. Spread in clean pan and mix with clean shovel or scoop.

3. Divide pile into four quarters.

4. Combine all material from two diagonal quarters, re-mix, and quarter again.

5. Mix one quarter and remove 1 pound sample.

6. Package in sealed polyethylene bag and place in one gallon paint can. Additional cans may be used if volume of sample is too large.

7. Mark each sample with all pertinent information, including if possible:

   a. Designation of material, manufacturer, batch No., Lot No., Bag No., Date manufactured, date received and any property data such as flow index listed on bag.

   b. Date sampled, NASA Langley formulation or control No., relative humidity and room temperature during sampling if available.

   c. Position in bag or drum from which the sample was taken, i.e., top, middle, bottom third, etc.

8. Pack polyethylene bag within can in vibration absorbing packing. Seal tightly and mail air freight or air parcel post.

Billet No. 2

Test Bulk Density

Replicate 1

Testing Specimen
Order Identification

	Axis Cut	Circum Cut	Radial Cut	Bulk Density G/cc
1	3	2	2	
2	1	1	3	
3	1	2	1	
4	2	2	2	
5	1	1	2	
6	3	2	3	
7	3	1	3	
8	2	3	1	
9	2	3	3	
10	3	1	1	
11	1	3	2	
12	2	2	3	
13	3	3	3	
14	2	3	2	
15	3	3	1	
16	3	2	1	
17	1	2	3	
18	1	2	2	
19	3	3	2	
20	1	3	1	
21	2	1	3	
22	1	3	3	
23	2	1	2	
24	1	1	1	
25	2	1	1	
26	3	1	2	
27	2	2	1	

Sample Data Sheet

APPENDIX IV

ANALYSIS OF VARIANCE

DENSITY STUDIES - BILLETS NO. 2 AND NO. 8

The cylindrical compression test specimens cut from each billet were also used for density determinations after thorough drying.

Analyses of variance were performed on the density data of both billets No. 2 and No. 8. In both analyses the same four factors were found to be highly significant (i.e., P equal 0.001 for all 8 cases). The four significant factors were:

1. Axial direction
2. Radial direction
3. Circumferential direction
4. Interaction of 1 and 2

Although it was of interest to determine the nature of the difference, if any, between the two billets, comparisons should not be made. Each billet had been machined into specimens and tested as soon as possible after receiving it. Thus trends or biases could invalidate comparisons.

In addition error variances of the two billets were incompatible (P equal 0.01). The error standard deviations were:

Billet	Standard Deviation
2	0.11 lb/cu ft
8	9.19

However obviously explanation and amplification of the results was required beyond the bare statement of significance of factors. To attain this end the following procedure was adopted. The mean response of each level of each significant factor, as measured form the billet mean, was calculated. Following this the 95% confidence interval of each mean response was calculated on the assumption that its standard

deviation was that shown above. (That is an analysis of variance model was assumed.) Thus the significance of the four factors could be interpreted in terms of clearly-defined non-coincident confidence intervals of their respective levels. In addition, although confidence levels could not be specified for such comparisons some appraisals of billet-to-billet differences could be made by considering the confidence intervals of corresponding factor levels. The results were:

Axial Direction

The 95% confidence intervals of the effects in pounds per cu ft were:

Axial Cut Sector	Billet 2		Billet 8	
	Low	High	Low	High
Top Disc	-.04	+.07	+.16	+.34
Middle Disc	-.51	-.40	-.52	-.34
Bottom Disc	+.38	+.49	+.09	+.27

(It should be emphasized that the above scatters apply to means of 18 readings. Scatters of individuals would be considerably wider.)

Note the "sandwich" effect. In each billet there is no over lap of the middle sector interval with that of either top or bottom sectors.

As mentioned above comparisons between billets are of doubtful validity. However although significance levels cannot be given, it is interesting to note that the confidence intervals of top discs do not overlap. This is also true of bottom discs but not of middle discs.

Radial Direction

The 95% confidence intervals of the effects in lbs per cu ft were:

Perpendicular Distance from Axis-inches	Billet 2		Billet 8	
	Low	High	Low	High
2.43	-.13	-.03	-.18	.00
4.21	-.12	-.01	-.23	-.05
5.44	+.09	+.20	+.14	+.32

The overlaps indicate that the two billets are alike with respect to this factor. The "case-hardening" at the outer radius is quite evident. The two inner radii values are coincident but there appears to be a discontinuity at or near the outer radius, i.e., the transition does not appear to be gradual.

It should be noted that there is an overlap of the intervals of both billets at each of the three radii. In this regard the two billets are indistinguishable.

Circumferential Direction

The 95% confidence intervals of the effects in lbs per cu ft were:

Angular Distance from Index degrees	Billet 2 Low	Billet 2 High	Billet 8 Low	Billet 8 High
0	+.07	+.18	+.09	+.27
120	-.08	+.03	-.24	-.06
240	-.16	-.05	-.12	+.06

In both billets the 120° and 240° intervals overlap but the 0° interval does not overlap either of the other two intervals. Thus once again as in the case of the radial effect there is a consistency prevailing from billet-to-billet. That is, although there is a within billet variability associated with angle, there is a tendency for the relationship to remain approximately constant from billet-to-billet.

Although not as in the case of the radial effect the intervals of corresponding factor levels of the two billets overlap.

Axial-Radial Interaction

The 95% confidence intervals of the effects in lbs per cu ft were:

Axial Cut Sector	Perpendicular Distance from Axis-inches	Billet 2		Billet 8	
		Low	High	Low	High
Top disc	2.43	-.04	+.15	-.07	+.24
Middle disc	2.43	-.39	-.21	-.39	-.08
Bottom disc	2.43	+.15	+.34	-.01	+.31
Top disc	4.21	-.12	+.06	-.19	+.12
Middle disc	4.21	-.20	-.02	-.25	+.07
Bottom disc	4.21	+.04	+.23	-.04	+.28
Top disc	5.44	-.12	+.07	-.21	-.10
Middle disc	5.44	+.32	+.50	+.17	+.48
Bottom disc	5.44	-.47	-.29	-.43	-.11

Inspection of the intervals reveals that in both billets at each of the two lower radii the middle is lower in density than either top or bottom. However at the outer radius the situation is completely reversed, viz., the middle is higher in density. Thus the interaction indicates that a billet can be approximated by a model consisting of a "high" density shell enveloping a "low" density core.

Note that the intervals of the billets overlap at each factor level.

The correlation coefficient is +0.81 which is highly significant (P less than .001). However it is evident that in addition to random scatter, bias is present.

Let us consider some implications of this viewpoint.

The density of a billet at each point can be considered to be a function of the vector representing the point. If the constants of the relationship are the same for both billets than corresponding densities will be alike except for random error and the plotted points will be distributed approximately equally on both sides of the dashed line. Figure A-8. If the intercepts are different and coefficients alike then the means of the densities will be different but the slope of the line will be unity. If both constants of the relationship are different this will be revealed by means being unequal and slope being different from 1.0.

The means are different (Billet 2, 33.70 lbs/cu ft and Billet 8, 33.50 lbs/cu ft).

The slope should not be estimated by the usual least squares technique because both variables (densities) are subject to error. Bartlett's method of means can be used to yield a value of +0.73.

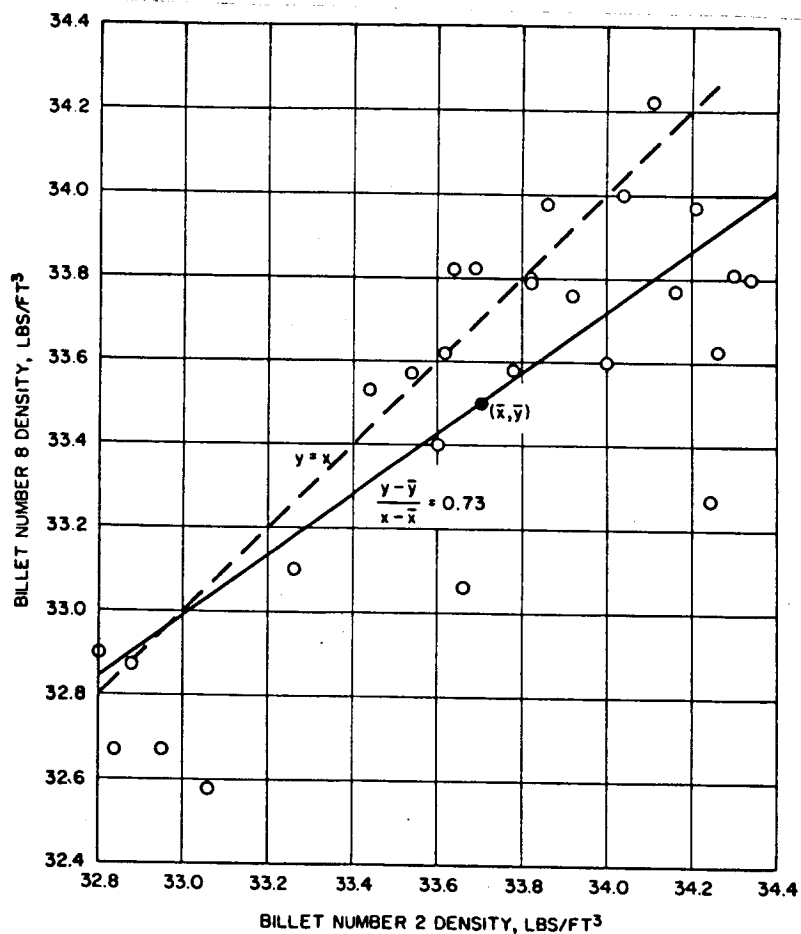Apparently the third condition most nearly represents the true situation.

Figure A-8. Densities of corresponding points within billets; means of two readings

APPENDIX V

SYNTHESIS OF PHENOLIC NOVOLACS

LABORATORY PREPARATIONS

Low Factor Novolac #1

A phenolic novolac was synthesized in the laboratory from high purity starting materials, so that a "standard" resin of a more or less well-known or easily defined chemical and physical characteristics would be available with which to compare the Bakelite material under investigation. Reagent grade phenol, uninhibited formaldehyde (celanese formaldehyde, 37% aqueous solution), and reagent grade oxalic acid (low in metal) were used in the following preparation; termed a "low factor novolac":

Phenol	200 g.
Formaldehyde 37% sol	136 g.
Oxalic Acid	2 g.

The ingredients were blended in an all glass resin reaction kettle fitted with a Teflon blade stirrer, thermometer, and reflux condenser. A Variac regulated mantle was used to heat the system gradually to water reflux temperature $(100-101^\circ C)$, which was maintained for a total of about 4 hours, with continuous stirring. No difficulties of the runaway "exotherm" type were experienced. pH of the reaction mixture was 0.9 at $25^\circ C$, as measured by a Beckman pH meter. At the end of the 4 hour period, a test of the aqueous phase of the heterogeneous reaction mixture was negative for formaldehyde (2,4-dinitrophenylhydraxine). Water was then distilled out of the system, with continuous stirring, until the reaction mixture temperature reached $160^\circ C$. The apparatus was dismantled, and the viscous, transparent water-white novolac was poured in a glass beaker to cool overnight to a brittle, glassy solid, easily powdered. Stored in a glass jar at room condition for 24 hours, this product, designated LFN-1 turned faintly pink. The product was

soluble in polar solvents (acetone, ethyl alcohol, MEK) but not in non-polar solvents (carbon tetrachloride, toluene).

An IR scan of the product examined as a film deposited on a NaCl window from acetone solution was virtually identical with a scan of the commercial resin, indication that the novolac has been very closely duplicated both as to composition and as to advancement of cure in the control synthesis attempt.

High Factor Novolac #1

In continuation of the synthesis program, a "high factor" phenolic novolac was prepared as follows:

Phenol	200 g.
Formaldehyde 37% aq. solution	144 g.
Oxalic Acid Approx.	2 g.

The reagent grade phenol and oxalic acid, the Celanese uninhibited formaldehyde, and the apparatus and procedures used were the same as those described in the previously reported "low factor" novolac preparation, except for the duration of the reaction "cook", which was approximately 2.5 hours. (In the "low factor" synthesis, the time was approximately 4 hours.) Essential completion of the reaction was indicated, as previously, by a negative dinitrophenylhydrazine test for formaldehyde. The product was finally recovered as a brittle water-white solid, very soluble in acetone. Total product yield was calculated as 213 g., of which 172 g. was recoverd as solid resin from the cooled reaction mass, the remainder being recovered in the form of a 27% acetone solution.

Low Factor Novolac #2

A second experimental low factor Novolac (LFN-2) was prepared, in an effort to obtain a resin with minimum inorganic ash. The reagents were the same as those used in the previous "cooks": MCB reagent phenol, Celanese inhibitor-free 37% formaldehyde, and reagent oxalic acid. However, in order to minimize contamination of the resin by the equipment, the glass reaction kettle and the thermometer, were

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boiled out with dilute hydrochloric acid solution, and the stirrer shaft and blade were rinsed with dilute nitric acid. All the parts so treated were finally rinsed with distilled water.

The reaction mixture consisted of:

Phenol	1000 g.
Formaldehyde, 37%	680 g.
Oxalic Acid	10 g. (added dry)

The materials were blended in the 3-liter resin kettle to a homogeneous water-white solution, pH 0.1 - 1.0. On heating, a rapid exothermic reaction developed, and an indeterminate quantity of material, chiefly formaldehyde violently boiled up through the condenser and was lost. The system was rapidly cooled down and allowed to come to room temperature. On the following day, it was decided to complete the run in order to obtain a resinous product which could at least be used for ash analysis. The reaction mixture was held at water reflux temperature for about one hour, until an opaque, milky product was formed. Finally, water was distilled out of the system, and the clear, nearly water-white, viscous product was poured into a Teflon-film lined tray to cool to a transparent, brittle, easily powdered solid. Total yield, approximately 850 grams.

High Factor Novolac #3

A second experimental high factor novolac (HFN-2), was prepared. The 3 liter reaction kettle and fittings used in the LFN-2 preparation, cleaned of all resin and reactants of the previous run by thorough solvent rinsing, was again "cleaned out" by boiling one liter of dilute H Cl (100 ml conc. acid/liter solution) for 2 hours at water reflux temperature. After this treatment, the apparatus was completely disassembled, and all parts were thoroughly rinsed with distilled water.

The reaction mixture consisted of:

Phenol	690 g.	(remainder of the MCB reagent phenol supply)
Formaldehyde (37%)	500 g.	(Celanese)
Oxalic acid	8 g.	

The materials were placed in the kettle; the stirrer, thermometer, and condenser were attached, and the system was allowed to stand at room conditions overnight. Next day, the system was heated cautiously to water reflux, with continuous gentle stirring, and maintained at a reaction temperature of 100 -101°C for about 2 hours. Water was then distilled off, with slow stirring, until the clear, nearly water-white fluid resin was isolated. On cooling in a Teflon-film lined pan, this was recovered as a 615-gram block, similar in appearance and frangibility to the previous products.

Low Factor Novolac #3

A fifth preparation was carried out (low factor Novolac #3 LFN-3) with the same apparatus and procedures. The only important difference in this run was the use of chemically pure phenol (National Aniline reagent).

The formulation was:

Phenol	800 g.
Formaldehyde (37%)	544 g.
Oxalic acid	8 g.

The resinous product as finally isolated was a transparent, amber colored, brittle solid. The color was evidently due to darkening of the phenol, which was seen to occur when the solid reagent was melted in its original glass container to facilitate pouring.

LARGE BATCH PREPARATION - HFN NOVOLAC

EQUIPMENT REQUIREMENTS

Stainless steel resin kettle of approximately 60 gallons capacity, with agitator, jacket or coils for cooling, condenser, and bottom discharge outlet. Should be capable of heating to at least 150°C with either steam or electric heaters.

Equipment for melting phenol, sufficient capacity to accommodate a 55 gallon drum.

Stainless steel weigh tank and scales.

Stainless steel or Teflon-coated shallow pans for resin discharge.

Drums for storing resin Beckman pH meter.

Micropulverizer.

Rotex for sizing.

NOVOLAC FORMULATION

60 gallon kettle charge synthetic Phenol (100%)	185 pounds
Formalin (37%, uninhibited)	133 pounds
Oxalic Acid	1.85 pounds
(840 g. or 13.3 g. equiv.)	

Yield about 200 pounds

PROCEDURE

Charge formalin and phenol into clean kettle.

Add oxalic acid to give pH of 0.5 to 1.0.

Heat charge cautiously to reflux at atmospheric pressure.

Control exotherm with cold water in jacket or occasionally vacuum refluxing with agitator running.

Continue atmospheric pressure refluxing until formaldehyde content is less than 1% of its initial value. Reflux time = 2 - 4 hours.

Remove water by distilling at atmospheric pressure with stirring.

When resin temperature reaches $160^{\circ}C$, pour batch into clean shallow steel pan to cool.

APPENDIX VI - MOLDING INVESTIGATION - SCOUT NOSE CAP

1.0 PLAN

The investigation will be carried out in three phases:

1.1 Molding of nose caps from ungraded raw materials, and commercial resin using Langley and HAC LAF No. 1 formulation.

1.2 Molding of nose caps from upgraded raw materials, commercial resin, using Langley and HAC LAF No. 1 formulation.

1.3 Molding of nose caps from upgraded raw materials and HAC HFN No. 4 resin using Langley and HAC LAF No. 1 formulation.

2.0 PRETREATMENT OF RAW MATERIALS

2.1 Powdered Nylon and Phenolic Microballoons

2.1.1 Tumble as received nylon and microspheres in tumbling barrel (1/2 full) for 3 mins.

2.1.2 Divide into approx. 1000 gm lots and package in individual polyethylene bags. Take 50 gm sample for moisture content. Place bags in sealed container.

2.1.3 Mark each bag with batch No. grade, moisture content, and approx. amount of material.

2.2 Phenolic Resin Commercial

2.2.1 Clean tumbling barrel by blowing out with air and wiping with clean rags. Fill approximately 1/3 full and tumble for 30 minutes with intensifier star in place. Sample 50 gm for moisture content analysis.

2.2.2 Repackage in approx. 1000 gm lots in individual polyethylene bags. Place bags in sealed container. Mark container with material name, batch number, tumbling treatment, moisture content, and approximate amount of material in each container.

3.0 PHASE I MOLDINGS

Phase I moldings will be made from un-graded raw materials. Two formulations will be used.

Based on dry wt.	Langley Formulation Wt-%	HAC LAF I Wt-%
Commercial Novolac	25.0	37.0
Phenolic Microspheres	35.0	23.0
Powdered Nylon -66 80 mesh	40.0	40.0

3.1 Formulation Procedure

3.1.1 Formulations will be mixed in the tumbling barrel using the star intensifier. No more than 12 pounds (5443 gm) will be mixed at one time.

3.1.2 Tumbling barrel charges will be as follows:

	Langley Formulation Wt-Gms	HAC LAF No. 1 Wt-Gms
Nylon	2177.0	2177.0
Microspheres	1905.0	1252.0
Commercial Novolac Corrected to dry wt.	1361.0	2014.0
Total Charge	5443.0	5443.0

3.1.3 Weigh materials to nearest gm. Weigh in polyethylene bags at all times. Correct material weights for moisture content as follows: (if moisture content is 3% multiply above weights by $\frac{103}{100}$ to obtain actual charge weight to be added to mix).

Calculate corrected weight for each material.

3.1.4 Add weighed charges to tumbling barrel from polyethylene bags by passing through a 20 mesh sieve placed over the opening of the barrel. Add nylon first, then microspheres, then resin. Seal

top of tumbler tightly and tumble for 30 minutes. Examine to see if uniform mix has been obtained. Tumble an additional 5 minutes if necessary to obtain uniform mix.

      3.1.5 Package formulation in polyethylene bags. Label with type of mix, and date mixed. Place bags in sealed containers.

4.0 MOLDING PROCEDURE - PHASE I

      4.1 Use two-12 pound mixes of Langley formulation as described in 3.1.1 to 3.1.5.

      4.2 Heat mold to $300 \pm 5^\circ$F. Continuously record thermocouple readings during molding. Set press load at 150 tons. Attach vacuum lines to mold.

      4.3 Clean mold, weigh out calculated charge wt. Based on dry weight of 1758 gms.

      4.4 Dielectrically preheat mix to soft consistency with CP 40A Preheater and place charge in mold without delay and without loss. Record dielectric preheat conditions.

      4.5 Close mold at medium speed with vacuum to full close. Cure at $300^\circ \pm 5^\circ$F for 3 hours. Remove part hot. If part blisters, cool subsequent parts to 200°F before removal.

      4.6 Place hot part on flat cardboard or fiberglass laminate, insulate with fiberglass or other fibrous insulator and allow to cool slowly.

      4.7 After cooling to room temperature, weight part. Adjust future charge weights to produce finished molding of 1708 gm cold weight.

      4.8 Make five additional nose caps as in 4.2 to 4.7 with suitable modifications as on preheat and cure procedure, and charge weight to produce uniform part. Scribe these parts in order on flat surface with I-L- numbers 1 to 6 for Langley Formulation, ungraded materials, HAC process. Inspect major dimensions.

4.9 Repeat above procedure (Para. 4.2 through 4.7) using two-12 pound mixes of HAC LAF No. 1 formulation as described in Para. 3.1.1 through 3.1.5. Modify preheat, charge weight, etc., to obtain uniform moldings weighing 1708 gm cold weight. Label parts I-H-numbers 1 to 6 for HAC LAF No. 1, ungraded materials, HAC Process. Inspect major dimensions.

5.0 POSTCURE

5.1 Place five cold parts on rack and place rack in sealed postcure canister. Attach the thermocouple to inside surface of center part and continuously record temperature.

5.2 Secure canister in Despatch oven, attach argon lines with inlet at top and flush out with nitrogen gas for five minutes.

5.3 Attach argon bottle, adjust flow rate to 40 cc/min.

5.4 Raise temperature from room temperature to 350°F in 12 hours, maintain for 6 hours. Cool to 100°F or less before removing parts. (Note: Make trial run with previously molded parts first in order to see if postcure is too severe).

5.5 Re-weigh parts, re-inspect major dimensions, and package in polyethylene bags.

6.0 PHASE TWO - UPGRADED RAW MATERIALS

6.1 Repeat above procedure Paras. 2 through 5 substituting 120 mesh nylon and screened Microspheres. Label parts II-L-Nos. 1 to 6 for Langley Formulation, Upgraded Materials, Hughes Process, and II-H-Nos. 1 to 6 for HAC LAF No. 1, Upgraded Materials Hughes Process.

7.0 PHASE THREE, UPGRADED MATERIALS AND HFN No. 4 RESIN

Substituting HAC HFN No. 4 resin for commercial novolac in Para. 6.0, repeat above procedure Paragraphs 2 through 5. Make 20 HAC LAF No. 1 parts instead of six. Label parts as follows:

II-L- Nos. 1 to 6 for Langley Formulation, Upgraded Raw Material, HFN No. 4, Hughes Process.

III-H- Nos. 1 to 20 for HAC LAF No. 1, Upgraded Raw Material, HFN No. 4, Hughes Process.

APPENDIX VII - MATERIAL SPECIFICATION

HUGHES MATERIAL SPECIFICATION (PRELIMINARY)

PHENOLIC MICROSPHERES

1.0 SCOPE

This specification covers the phenolic microspheres used in compounding the molding mix for syntactic foam ablative material.

2.0 APPLICABLE DOCUMENTS

3.0 REQUIREMENTS

3.1 Qualifications

3.1.1 The phenolic microspheres shall be a product that has passed the qualification tests described in Section 4.3.

3.2.1 There shall be two types of materials as follows:

Type I - As received

Type II - Sieved and upgraded

3.2 Physical Properties

3.2.1 Particle Size Distribution. The particle size distribution shall meet the following requirements when subjected to the sieve analysis in accordance with Section 4.3.1.

Type I - As received from manufacturer

Type II - U.S. Sieve No.	% Retained (Min.)	% Passes (Max.)
50	0	100
120	25	80
170	25	40
230	25	0

3.2.2 Volatile Content. The volatile content shall not exceed 5 percent when tested in accordance with 4.3 2.

3.2.3 <u>True Density.</u> The true density shall lie as follows when tested in accordance with 4.3.3.

$$\text{Type I} - 15.0 \pm 3.0 \text{ lbs/ft}^3$$
$$\text{Type II} - 15.5 \pm 1.5 \text{ lbs/ft}^3$$

4.0 QUALITY ASSURANCE PROVISIONS

4.1 <u>Sampling.</u> The following sampling procedure shall be applicable.

4.1.1 <u>Sampling Plan.</u> Each drum shall be sampled from three distinct locations as follows: Top, bottom, and center. A 150 gram sample shall be removed from each location.

4.2 <u>Procedure (note for Type II).</u> All of the material shall be passed through a U.S. Sieve No. 50 mesh screen. Any material which remains on the 50 mesh screen shall be eliminated. All of the material shall remain on a U.S. Sieve No. 230. Any material which passes through the 230 mesh screen shall be eliminated.

4.3 <u>Particle Size.</u> The qualification tests shall be as follows:

4.3.1 <u>Particle Size.</u> The test for particle size distribution shall be made using standard U.S. Sieves and a Rot-A-Tap mechanical shaker or its equivalent. The sieves listed in paragraph 3.2.1 shall be used with a cover and a bottom pan; with the No. 50 at the top and the 230 at the bottom. 25 grams ± 0.1 grams of the microspheres shall be poured onto the No. 50 sieve screen, the cover put into place and the assembly allowed to shake for 15 ± 1/2 minutes. Following the shaking the material retained on each sieve shall be separately removed and weighed to the nearest 0.01 gram; the percentage of material retained in each sieve screen shall be computed as follows:

$$\text{Percent retained} = \text{grams of material retained divided by total recovered material}$$

The percentage passed by each screen shall be the total percentage retained on all the sieves below it in the sieve assembly; for example the percentage passed by the U.S. No. 50 screen would be calculated as follows:

Percent passed by US No. 50 screen = percent retained on
US No. 120, plus, percent retained on
US No. 170, plus percent retained on
US No. 230

4.3.2 <u>Volatile Content.</u> The volatile content of the micro-
spheres shall be run on triplicate samples of 1 gram ± 0.1 gram; the
samples shall be weighed to 0.0001 grams; the tare of a crucible shall
be weighed. The sample shall be weighed (W_1), then dried in a
mechanical convection oven at $300°F$ for $30 ± 2$ minutes, and reweighed
(W_2). The volatile shall be calculated as follows:

$$\text{Percent volatile matter} = \frac{(W_1 - W_2)}{W_1} \times 100 \quad .$$

4.3.3 <u>True Density.</u> The true density of the microspheres
shall be run in duplicate samples. Determine the weight of the empty
Pycnometer to the nearest 0.001 gram. Determine the weight of the
Pycnometer filled with analytical reagent grade Toluene containing
0.1% Duponol G by weight. Determine the density of at least 100 ml of
the Toluene-Duponol G mixture. Fill lower chamber of dry Pycnometer
approximately half full of microspheres which have been dried for
18 hours at $120°F$. Determine the weight of the pycnometer and
microspheres. With pycnometer in vertical position, add Toluene-
Duponol G mixture carefully until no air bubbles remain. Weigh
pycnometer with microspheres and Toluene. Calculate the true density
with the following:

$$\text{True density} = \frac{W_m D_t}{W_t W_m}$$

W_m = Weight of microspheres

D_t = Density of Toluene-Duponol G mixture

W_t = Weight of the Toluene without microspheres

W_{tm} = Weight of Toluene with microspheres present

HUGHES MATERIAL SPECIFICATION (PRELIMINARY)

RESIN - PHENOLIC NOVOLAC

1.0 SCOPE

1.1 This specification covers dry powdered phenolic novolac resin for use in the formulation of low density ablative foam.

1.2 Classification

Resin included in this specification is classified in two types.

Type I - Commercial

Type II - Highly characterized phenolic

2.0 APPLICABLE DOCUMENTS

HMS 16-1096, Glass Fabric, Impregnated with Phenolic Resin

3.0 REQUIREMENTS

3.1 Qualification

The phenolic novolac resin furnished under this specification shall be products which have passed the qualification tests in Table I. when tested in accordance with Section 5.

	Type I	Type II
Total Volatile Content	5% max.	5% max.
Viscosity Number	2.1-2.3	2.1-2.3
Ash Content	0.080% max.	0.080% max.
Particle Size	-325 Mesh	-250 Mesh
Water Extractable-% (including Hexamethylenetetramine	16% max.	14% max.
Cure Time - seconds	110.140	110-140

4.0 SAMPLING AND TEST PROCEDURES

4.1 <u>Sampling</u> - The following sampling procedure shall be applicable.

4.1.1 <u>Sampling Plan</u> - Each drum shall be sampled from three distinct locations as follows: Top, bottom, and center. A 150 gram sample shall be removed from each location.

4.2 <u>Test Procedures</u>

4.2.1 <u>Volatile Content.</u> - the volative content of the microspheres shall be run on triplicate samples of 1 gram ± 0.1 grams; the samples shall be weighed to 0.0001 grams; the tare of a crucible shall be weighed. The sample shall be weighed (W_1), then dried in a mechanical convection oven at 300°F for 30 $\pm$2 minutes, and reweighed (W_2). The volatile matter shall be calculated as follows:

$$\text{Percent volatile matter} = \frac{(W_1 - W_2)}{W_1} \times 100$$

4.2.2 <u>Viscosity Number</u> - Test as described in HMS 16-1096.

4.2.3 <u>Ash Content</u> - Test as in 4.2.1 except that the dry sample from the volatile content test shall be subjected to 1300°F until it reaches constant weight within ± 0.0001 grams. Ash content shall be calculated on the basis of dry weight of resin.

4.2.4 <u>Particle Size</u> - All material shall pass the designated sieve size when tested using standard U.S. sieve and Rot-A-Top machine or equivalent. A 25 gram sample shall be used.

4.2.5 <u>Water Extractables</u> - A 25 gram sample of resin shall be washed and filtered six times in approximately 1 quart of distilled water. The individual washings shall be for 2 hours with water at 80-110°F in a Waring Blender set for high speed mixing. The washed material after the six washings shall be dried to constant weight in a vacuum oven at 120°F.

4.2.6 <u>Cure Time</u> - A 0.05 gram sample of resin shall be placed with a spatula on a hot plate controlled to a temperature of $302^{\circ} \pm 2^{\circ}F$. A stop watch shall be used to determine the cure time. Cure shall be completed when the material no longer strings with the spatula.

5.0 APPROVED MATERIALS

Type II - Hughes HFN phenolic novolac resin.

NYLON - POWDERED

1.0 SCOPE

1.1 Scope - This specification covers the nylon used in compounding the molding mix for syntactic foam ablative material.

2.0 APPLICABLE DOCUMENTS

2.1 There are no applicable governmental documents.

3.0 REQUIREMENTS

3.1 Qualifications - The nylon shall be a type 66 that has passed the qualification tests described in section 4.3.

3.2 Classes - There shall be two classes of material as follows:
Class A - Average Particle Size 80 mesh
Class B - All particles shall pass through 120
mesh screen.

3.3 Physical Properties

3.3.1 Particle - The particle size distribution shall meet the following requirements when subjected to the sieve analysis in accordance with 4.3.1. The two classes of material shall be defined as specified in 3.2.

3.3.2 Ash Content - The ash content shall not exceed 0.6 percent when tested in accordance with 4.2.2.

3.3.3 Melting Point - The melting point shall lie between 250°C and 260°C when tested in accordance with 4.2.3.

4.0 QUALITY ASSURANCE PROVISIONS

4.1 Sampling - The following sampling procedure shall be applicable.

4.1.1 <u>Sampling Plan</u> - Each drum shall be sampled from three distinct locations as follows: Top, Bottom, and Center. A 150 gram sample shall be removed from each location.

4.2 <u>Qualification Tests</u> - The qualification tests shall be as follows:

4.2.1 <u>Particle Size</u> - The test for particle size distribution shall be made using standard U.S. Sieves and a Rot-A-Tap mechanical shaker or its equivalent. The sieves shall be used with a cover and a bottom pan; with a No. 50 at the top a No. 120, a No. 17 and the 230 at the bottom. 25 grams $\pm$0.1 grams of the nylon shall be poured onto the No. 50 sieve screen, the cover put into place and the assembly allowed to shake for 15 $\pm$1/2 minutes. Following the shaking the material retained on each sieve shall be separately removed and weighed to the nearest 0.01 gram; the percentage of material retained in each sieve screen shall be computed as follows:

Percent retained = Grams of material retained divided by total recovered material.

The percentage passed by each screen shall be the total percentage retained on all the sieves below it in the sieve assembly; for example the percentage passed by the U.S. No. 50 screen would be calculated as follows:

Percent passed by U.S. No. 50 screen = Percent retained on U.S. No. 120, plus, percent retained on U.S. No. 170, plus, percent retained on U.S. No. 230.

The 40 to 60 percentile marks of the distribution should all be contained on the 120 mesh screen.

4.2.2 <u>Ash Content</u> - The ash content of the nylon will be run on triplicate samples of 30 grams ±0.5 grams. The samples shall be weighed to 0.001 grams; the tare of the crucible shall be weighed. The sample shall be placed in an oven controlled at a temperature of $1300^{\circ}F$ $\pm10^{\circ}F$, for a period of one hour. The ash content shall be calculated as follows:

$$\text{Percent Ash} = \frac{W_o - W_f}{W_o} \times 100$$

where W_o = Original weight of sample

W_f = Final weight of sample

4.2.3 <u>Melting Point</u> - The melting point of the nylon shall be run in triplicate. The Fisher-Johns melting point apparatus shall be employed. A sample of 0.05 grams shall be placed between two glass covers and placed on the stage of the apparatus. Heat shall be applied to the stage at a rate of $10^{\circ}C$ per minute. The melting point observed shall be recorded to the nearest degree.